LOW-SULFUR LIQUID FUELS FROM COAL

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INTRODUCTION

Coal combustion is a major source of sulfur dioxide, and since electric utilities are the major consumers of coal, power generating stations are the principal points of origin for this pollutant.[1] Consequently, the air pollution regulations designed to check the emission of sulfur dioxide concern the electric utilities. The sulfur dioxide abatement regulations of many communities translate to a permissible concentration of 0.3 - 1.0 percent sulfur in fuels,[2] with 0.7 a common limit. This level of sulfur is too low for most of the coal that has been consumed by power generating stations to be permissible fuels.[3] The present work describes a method for producing an acceptable low-sulfur utility fuel by hydrodesulfurizing coal catalytically in a continuous fixed-bed reactor.

The reaction of coal with hydrogen has been studied extensively in the past with the objective of producing gasoline and special fuel oils.[4,5,6] At elevated temperatures and pressures and in the presence of suitable catalysts, coal reacts with hydrogen to give a mixture of liquid and gaseous hydrocarbons and the heteroatoms in coal are eliminated as hydrides. The initial liquid hydrocarbon products may then be upgraded to gasoline or other high grade fuels but an item of major cost in the process is hydrogen. Coals contain about 5 percent hydrogen, gasoline about 14 percent, and many fuel oils about 9-11 percent. Thus, large quantities of hydrogen, an expensive gas, are required to produce gasoline or such oils from coal. However, detailed considerations of past data reveal that the consumption of hydrogen in the primary liquefaction of coal is small; the bulk of the hydrogen is consumed in upgrading the products of primary liquefaction. A solution to the fuel problem of the electric utilities may, therefore, be found by limiting the hydrogenation of the coal to the primary liquefaction step only, making desulfurization with minimal hydrogen consumption the exclusive objective. The expenditure of hydrogen on the primary liquefaction of coal is of course unavoidable because of the molecular alterations associated with removal of bound sulfur; however the far larger expenditure of hydrogen in upgrading the products of primary liquefaction to even lower molecular weights may be eliminated.

The work of this report shows that the reaction of coal with hydrogen may be conducted under select conditions that promote desulfurization but minimize additional hydrogenation of the products from the primary liquefaction. The relatively viscous liquid product may then be used as a low-sulfur utility fuel either directly or after further physical refinement by removal of the ash and unreacted coal, depending on the design of the furnace to be fired with it. An ash-free fuel is of considerable benefit to some furnace-boiler or even turbo-engine installations.

Hydrodesulfurization of a tar slurry of coal containing 3.4 percent sulfur to yield a fuel having 0.3 percent sulfur at 4,000 psig was described in our earlier publication.[9] It has now been found that fuel oils containing an equally low level of sulfur are obtained at the more economical conditions of reduced pressure of 2,000 psig and shorter residence time when the product is centrifuged and recycle oil is used instead of tar as feed vehicle. Complete solids removal would yield oils of only 0.18 percent sulfur from this coal at these conditions. The yields and chemical and physical properties of desulfurized synthetic fuel oils from three different coals are detailed in this report.

EXPERIMENTAL

Basically, to effect hydrodesulfurization without unnecessary hydrogenation, a short residence time in a packed-catalyst-bed reactor is used. Conditions are highly turbulent to prevent plugging and to assist catalysis. Extensive engineering details concerning plant operations and selection of conditions have been presented elsewhere;[10] thus a brief description of the experimental approach suffices here.

Plant and Procedure. Figure 1 is a simplified diagram of the hydrodesulfurization plant. The reactor was a 68-foot long tube of 5/16-inch id, folded into 3-1/2 hairpin loops to fit inside a vertically placed, 10-foot long, cylindrical furnace of 10-inch id. The reactor was charged with about 2 lb of a commercial Co-Mo/SiO_2-Al_2O_3 catalyst. The feed stream of coal slurry in high-temperature tar and hydrogen passed through a preheater before entering the reactor from the bottom end. The product stream leaving the reactor at the top end was led through a water-cooled condenser to a high-pressure receiver for liquid products. The liquids and unreacted solids were collected in this receiver from where they were intermittently discharged into a vessel at atmospheric pressure. The gases leaving the receiver were passed through a second condenser and a second high-pressure receiver to ensure condensation and collection of any low-boiling product not retained in the first receiver. It may be mentioned, inter alia, that in the series of runs described in this paper, no liquid was collected in the second high-pressure receiver. The gas stream was scrubbed with alkali solution to remove H_2S and NH_3, then finally reduced to atmospheric pressure, metered, sampled, and flared. In multiple-pass experiments, the products were reintroduced into the reactor for as many repeated hydrotreatments as desired.

Since a commercial operation will almost certainly be conducted with slurries of coal in a portion of the steady state liquid generated in the process itself, the hydrodesulfurization of coal in a vehicle of coal-derived liquid was also studied. The coal-derived liquid was prepared by conducting a 4-cycle hydrodesulfurization experiment in which the feed for the first cycle was a slurry of 30 wt pct coal in tar while the feeds for the second, third, and fourth cycles were slurries of 30 wt pct coal in the centrifuged liquid products from the preceding cycle. It is estimated that the centrifuged liquid products from the fourth cycle contained at least 80 percent coal-derived liquids.

For secondary reasons, continuous operation of the plant was limited to a maximum of 12 days after which the plant was shut down for 2 days. Each run was started with a newly made reactor charged with fresh catalyst.

Sampling of the Products and Analysis. The liquid products from 25 lb of slurry feed were collected in a batch and sampled for analysis. Benzene insolubles, asphaltenes, and oils were determined by conventional solvent analysis: asphaltenes are soluble in benzene but insoluble in pentane, whereas oils are soluble both in benzene and pentane. Ash was determined by igniting the benzene insolubles. The concentrations of sulfur in the total liquid products and in the benzene insolubles, asphaltenes, and oils separately were determined by the Bomb-Washing Method.[7] The distribution of pyritic, organic, and sulfate sulfurs in the benzene insolubles was determined by the method recommended for the determination of forms of sulfur in coal.[8] The sulfur in asphaltenes and oils was assumed to be all organic.

Samples of the tail gas were analyzed periodically by gas chromatography to determine the formation of gaseous hydrocarbons. A small amount of methane is made.

Materials. Analyses for the three different feed coals and the high-temperature tar used in this work are presented in table 1. The coals were ground to pass 100 percent through a 14-mesh U.S. Standard sieve and 70 percent through a 200-mesh sieve. The high-temperature tar was derived from the coking of metallurgical grade bituminous coal and had been topped to 400° C by the suppliers, Koppers Co., Inc.* The $Co\text{-}Mo/SiO_2\text{-}Al_2O_3$ catalyst was purchased from Harshaw Chemical Co. (Manufacturer's identification number: 0402T).

RESULTS AND DISCUSSION

Hydrodesulfurization of Coal Using High-Temperature Tar as Vehicle. The results from the hydrodesulfurization of three different coals in a vehicle of high-temperature tar at 2,000 psi and 450° C are presented in tables 2 and 3. The tar was a useful facsimile of recycle product oil until it became available. In tar, Pittsburgh seam coal containing 1.3 percent sulfur was desulfurized to a fuel containing 0.3 percent sulfur, an Indiana #5 seam coal containing 3.4 percent sulfur was desulfurized to a fuel containing 0.42 percent sulfur, and a Middle Kittanning #6 seam coal containing 3.0 percent sulfur was desulfurized to a fuel containing 0.36 percent sulfur. In each case, the ash in the feed remained quantitatively in the products. The calorific value of the products from the three coals were about the same, 16,400 Btu/lb. About 284 scf of H_2 was consumed in processing 100 lb of the feed prepared from Pittsburgh seam coal, 304 scf of H_2 in processing 100 lb of feed prepared from the Indiana #5 seam coal, and 330 scf of H_2 in processing 100 lb of feed prepared from Middle Kittanning #6 coal. These figures for the consumption of hydrogen were calculated from the analyses of the feeds and the products and the yields of the liquid and gaseous products. The eliminated sulfur was assumed to be in the form of H_2S and nitrogen as NH_3. The consumption of hydrogen for reaction with oxygen was calculated by assuming total elimination of oxygen from the product. Determinations of oxygen by difference supports this assumption. In view of expected inaccuracies, these indirect figures should be considered only approximately indicative of the hydrogen requirement for the process. The plant is being modified to measure the consumption of hydrogen directly.

From the additional properties of the products listed in table 3, it is seen that the viscosities of the products from the two high-sulfur coals are lower than the viscosity of the products from Pittsburgh seam coal. It appears that the lower grade coals hydrogenate more extensively.

None of the products in table 3 contained components distillable below 200° C and the fraction distillable below 355° C was about the same, 20 percent by weight for each of the products.

Hydrodesulfurization of Coal in a Vehicle of Coal-Derived Liquid and the Properties of the Products Before and After Centrifugation. Tables 2 and 3 also contain the results from the hydrodesulfurization of Middle Kittanning #6 coal in a vehicle of coal-derived liquid (recycle oil). It may be noted that these results refer to a one-pass hydrotreatment of the feed compared to three-pass hydrotreatments of the feeds prepared in high-temperature tar. Thus the residence time is only one-third of that used for the tar slurry feeds. The concentration of sulfur in the products was 0.48 percent before centrifugation and 0.31 percent after centrifugation. The centrifugation residues amounted to about 9.5 percent by weight of the whole liquid products, and consisted of 33 percent organic benzene

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* References to specific brands of materials are made for identification only and does not imply endorsement by the Bureau of Mines.

TABLE 1.- Analyses of the feed coals and feed tar, as received

	hvab Pittsburgh seam coal	hvbb Indiana #5 seam coal	hvbb Middle Kittanning #6 seam coal	High-temperature tar
Proximate analysis, wt pct				
Moisture	1.0	6.1	2.4	-
Ash	11.1	8.9	9.4	-
Volatile matter	33.7	38.6	39.2	-
Fixed carbon	54.2	46.4	48.6	-
Ultimate analysis, wt pct				
Moisture	1.0	6.1	2.4	-
Ash	11.1	8.9	9.8	0.7
Carbon	73.5	67.0	71.0	92.3
Hydrogen	4.9	5.3	5.2	4.9
Nitrogen	1.4	1.4	1.3	1.2
Oxygen, by difference	6.8	7.9	7.3	0.3
Sulfur	1.3	3.4	3.0	0.6
as sulfate	0.07	0.37	0.01	-
as pyrite	0.60	0.98	1.28	-
as organic	0.63	2.07	1.71	0.6
Solvent analysis, wt pct				
Benzene insolubles	-	-	-	14.0
Asphaltenes	-	-	-	39.6
Oil	-	-	-	46.4
Heat content, Btu/lb	13,320	11,750	12,540	16,260

TABLE 2.- Hydrodesulfurization of coal slurries at 450° C and 2,000 psi
Slurry feed rate: 5 lb/hr
Hydrogen feed rate: 500 scfh

Feed	Gross Oil Product Analysis			
	S, wt pct	Ash, wt pct	Calorific value, Btu/lb	H_2 consumed, scf/100 lb of feed
30 wt pct Pittsburgh seam coal in tar[1]	0.3	1.5	16,450	284
30 wt pct Indiana #5 seam coal in tar[1]	0.42	2.7	16,415	304
30 wt pct Middle Kittanning #6 seam coal in tar[1]	0.36	2.5	16,310	330
30 wt pct Middle Kittanning #6 seam coal in coal-derived liquid,[2]				
before centrifugation	0.48	3.5	16,200	139
after centrifugation[3]	0.31	1.3	16,840	-

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[1] 3-pass hydrotreatment.
[2] 1-pass hydrotreatment.
[3] Centrifuge cake = 9.5 percent of gross product.

TABLE 3.- Some additional properties of the products from hydrodesulfurization of coal slurries at 450° C and 2,000 psi

Slurry feed rate: 5 lb/hr

Hydrogen feed rate: 500 scfh

Feed	Products						
	Sp. gr., 60°/60° F	Viscosity, SSF at 180° F	C, wt pct	H, wt pct	N, wt pct	Distillable fraction, wt pct	
						<200° C	<355° C
30 wt pct Pittsburgh seam coal in tar[1]	1.199	55	90.5	6.1	1.0	0.0	21.0
30 ey pct Indiana #5 seam coal in tar[1]	1.188	26	89.8	6.3	0.8	0.0	23.6
30 wt pct Middle Kittanning #6 seam coal in tar[1]	1.191	40	89.6	6.3	0.8	0.0	18.2
30 wt pct Middle Kittanning #6 seam coal in coal-derived liquid,[2]							
before centrifugation	1.148	101	84.9	7.4	0.9	0.0	27.5
after centrifugation[3]	1.135	135	88.4	7.5	0.9	-	-

[1] 3-pass hydrotreatment.

[2] 1-pass hydrotreatment.

[3] Centrifuge cake = 9.5 percent of gross product.

insolubles, 28 percent ash, 9 percent asphaltenes, and 30 percent oil. As may be expected, the specific gravity of the products was lower after centrifugation than before, but the viscosity of the products was surprisingly higher after centrifugation than before. This was probably due to atmospheric oxidation of the products during storage prior to centrifugation and during centrifugation. As is known, products of coal hydrogenation are sensitive to atmospheric oxidation.

It is interesting to note from table 2 that H_2 consumption drops remarkably when recycle oil is the vehicle instead of tar. As expected, the recycle oil is not as susceptible to further hydrogenation as tar is to initial hydrogenation.

Forms and Distribution of Sulfur in the Products. The forms and distribution of sulfur in the products from the hydrodesulfurization of Middle Kittanning #6 seam coal in high-temperature tar are presented in table 4. Similar data for products from the same coal processed in recycle oil have not been completed at this writing. The concentrations of sulfur in the benzene insoluble, asphaltene, and oil fractions of the products were determined separately. The bulk of the residual sulfur is always contained in the benzene insoluble fraction. This fraction, amounting to 13.2 percent of the products, contained 1.54 percent sulfur. The asphaltene and the oil fractions, which amounted to 21.7 and 65.1 percent of the products respectively, each contained 0.18 percent sulfur.

Thus it is clear that, if complete removal of the benzene insolubles could be obtained, theoretically 87 percent of the products may be recovered as an ash-free liquid containing only 0.18 percent sulfur. Aside from its premium quality as a fuel, such a liquid may be a valuable raw material for electrode carbon and to fuel turbine engine electric generators.

A determination of the forms of sulfur in the benzene-insoluble fraction revealed that 88 percent of the sulfur in it was organic, 7 percent pyritic, and 5 percent sulfate. The sulfur in the asphaltene and oil fractions may be assumed to be all organic. Thus, the total product contained 0.34 percent organic sulfur and only 0.01 percent each of pyritic and sulfate sulfurs. Since the feed contained 0.38 percent pyritic and 0.93 percent organic sulfur, the pyritic sulfur is evidently eliminated preferentially.

Data reported previously[9] showed that the fuel oil product from Pittsburgh seam coal could have a sulfur content as low as 0.09 percent if the benzene insolubles and ash are removed.

Yields. As is known, the concentrations of moisture, sulfur, and oxygen vary widely in coals. Removal of sulfur is of course the objective of the process, but the desulfurization is necessarily accompanied by removal of moisture and oxygen. Thus, yields of desulfurized fuels from coal may vary widely. If the desulfurized products are centrifuged, the yield of the centrifuged fuel will also vary with the concentration of mineral matter in coal. Evidently, a statement of yield will be meaningless unless accompanied by a statement of the maximum theoretical yield for each coal.

But even if the cumbersome practice of reporting yields together with the maximum theoretical yields is adopted, an important feature of the process will remain masked. The calorific values of the products are higher than the calorific values of the feeds, and despite mass losses in processing, the available heat from the products is frequently more than the available heat from the feeds. Thus, the heat content yields may be more than 100 percent even though the mass yields are less than 100 percent. Since for evaluating a fuel-making process

TABLE 4.- Forms and distribution of sulfur in the products from hydrodesulfurization of 30 wt pct Middle Kittanning #6 seam coal in tar

S, wt pct, in	
Benzene insolubles (13.2% of Prod.)	1.54
Asphaltenes (21.7% of Prod.)	0.18
Oil (65.1% of Prod.)	0.18
Forms of S, wt pct, in the benzene-insoluble fraction	
Sulfate	0.11
Pyritic	0.07
Organic	1.36
Forms of S, wt pct, in the total liquid products, assuming all S in asphaltenes and oil to be organic	
Sulfate	0.01
Pyritic	0.01
Organic	0.34
Total	0.36
S, wt pct, in the total liquid products by direct determination	0.38

the relevant yield is obviously the heat content yield, the following discussion will be in terms of Btu yields.

Generally, Btu yields in excess of 100 percent, when based on the liquid feed input, are explained thus: Hydrocracking reactions that produce lower molecular weights are slightly endothermic and absorb energy from the reactor system; more important, additional hydrogen is added to raise the calorific value.

From the figures presented in table 5, it will be seen that the Btu yields for the products from the hydrodesulfurization of coals in high-temperature tar are, in each case, in excess of 100 percent. The Btu yield for the hydrodesulfurization of Middle Kittanning #6 coal in coal-derived oil is 97 percent before centrifigation and 91 percent after centrifugation. It may be emphasized that the figures refer to the yields based on total feed, not coal alone. High-temperature tar also undergoes hydrotreatment and so does the recycle oil but not as extensively as tar. Therefore, the Btu yield appears lower for the recycle system.

SUMMARY AND CONCLUSIONS

It has been demonstrated that liquid fuels containing 0.3 percent sulfur may be prepared in entirety from coals containing 3.0 - 3.4 percent sulfur by catalytic hydrodesulfurization in a continuous fixed-bed operation at 450° C and 2,000 psi, followed by centrifugation of the products. The Btu yield of the centrifuged fuel is 91 percent. In areas where air pollution regulations are less stringent, the direct product of hydrodesulfurization may be used as a fuel without centrifugation. Such product contains 0.4 - 0.5 percent sulfur and its Btu yield is 97 - 102 percent. The desulfurized synthetic fuels are liquid at or near ambient temperature, suitable for direct use in oil-fired burners.

The residual sulfur in the products is essentially entirely of organic nature and the bulk of it is contained in the benzene-insoluble components. Because the product is liquid at low temperatures without significant volatility, solids separation should be relatively easy, to yield an ashless, very low-sulfur fuel oil.

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TABLE 5.- Yields of desulfurized fuels

Feed	Calorific value of feed, Btu/lb	Product		
		Exptal. Yield, wt pct	Calorific value, Btu/lb	Yield, Btu pct
30 wt pct Pittsburgh seam coal in high-temperature tar	15,378	94	16,450	100.6
30 wt pct Indiana #5 seam coal in high-temperature tar	14,907	93	16,415	102.4
30 wt pct Middle Kittanning #6 seam coal in high-temperature tar	15,144	94	16,310	101.2
30 wt pct Middle Kittanning #6 seam coal in coal-derived liquids,	15,550			
before centrifugation		93	16,200	96.9
after centrifugation		84	16,840	91.0

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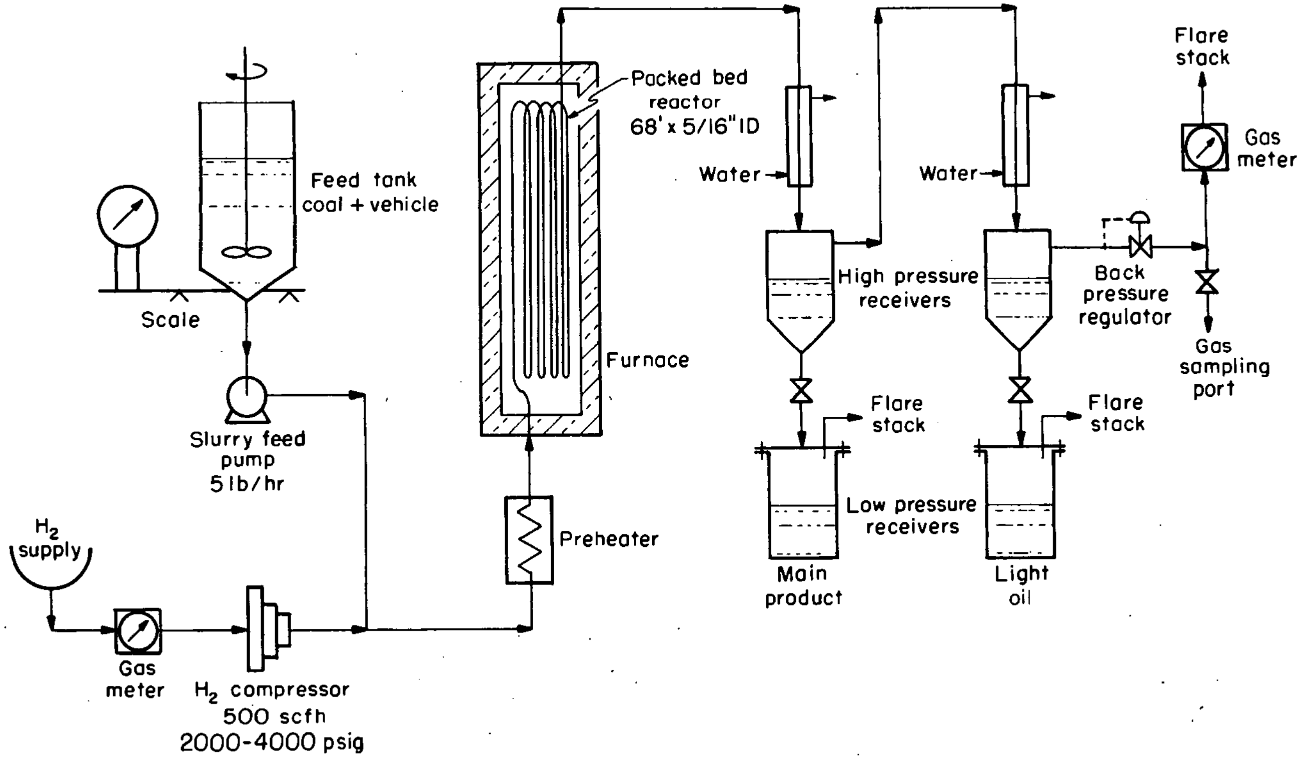
Feed tank
coal + vehicle
Scale
Slurry feed
pump
5 lb/hr
H_2
supply
Gas
meter
H_2 compressor
500 scfh
2000-4000 psig
Preheater
Furnace
Packed bed
reactor
68' x 5/16" ID
Water
Water
High pressure
receivers
Flare
stack
Flare
stack
Low pressure
receivers
Main
product
Light
oil
Back
pressure
regulator
Gas
meter
Flare
stack
Gas
sampling
port

Figure 1—Simplified schematic diagram of hydrodesulfurization pilot plant.

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USE OF A REFINERY LP MODEL TO DETERMINE VALUE OF COAL DERIVED LIQUID

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INTRODUCTION

Conversion of coal to a synthetic liquid product has been studied experimentally for a number of years. Because such processes appear to be moving closer to commercial reality, the economics of these processes have received more emphasis in recent years. One of the major problems in determining the economics of coal conversion processes involves settling on a value for the coal-derived liquid. In some economic studies a price has been estimated for this liquid based solely on the cost of producing it, including an arbitrary profit. Other studies, on the other hand, have tried to estimate a value for the coal-derived liquid on the basis of one or more inherent properties, or have used a somewhat arbitrary value.

In actual practice, however, the value of a feed stock to a refinery depends primarily upon the value of the products which can be made from it and the costs of processing to make such products. In the case of coal-derived materials, which have unusual characteristics compared to most crude oils, this is believed to be the most realistic method of estimating its value. This paper reports the results of such calculations made for a liquid produced in a conceptual coal conversion complex utilizing several experimental processes now being developed under sponsorship of the Office of Coal Research, U.S. Department of the Interior.

SOURCE OF COAL DERIVED LIQUID

This complex which produces the coal-derived liquid has been designated a COG (Coal, Oil, Gas) Refinery, since the two major products it produces from coal are the liquid feedstock to a petroleum refinery and a high BTU synthetic natural gas. The primary conversion step of this complex utilizes the Pittsburg & Midway Coal Mining Co's Solvent Refined Coal (SRC) process. Chem Systems has recently completed an economic evaluation of this complex for P&M.

An overall flowsheet for the COG Refinery is shown in Figure 1. The following processing steps are included:

- SRC Process - This is the primary coal conversion step where coal is dissolved in the presence of a process solvent and hydrogen at high temperatures (~825°F) and pressures (~1000 psia). The reaction product is filtered to yield solvent refined coal, a low sulfur de-ashed product. Filter cake, containing undissolved coal and ash is sent to the gasification section. A light oil, C_5-450°F and gases, C_1-C_4, are also produced in the SRC process.

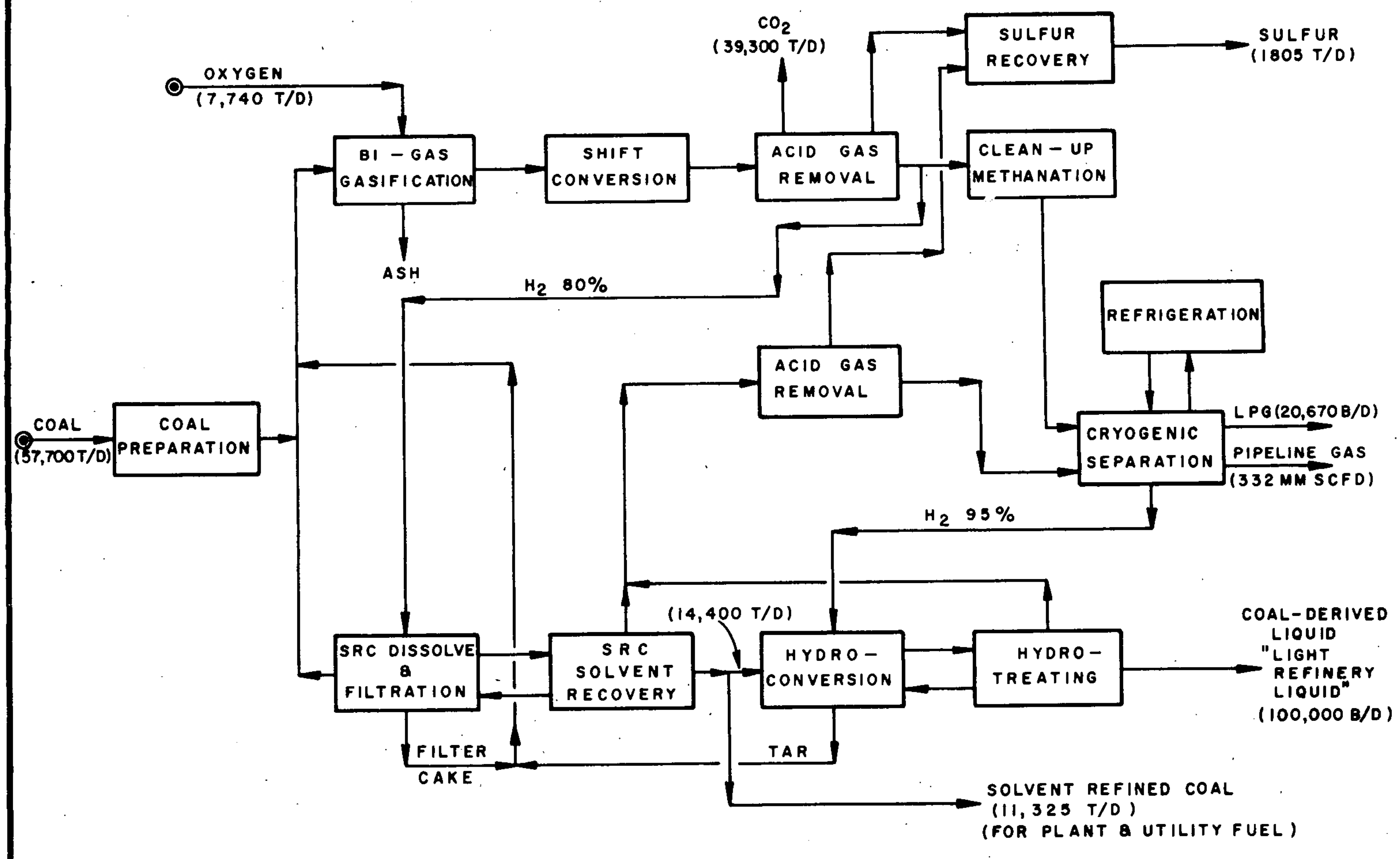
OXYGEN
(7,740 T/D)
COAL
(57,700 T/D)
COAL PREPARATION
BI – GAS GASIFICATION
ASH
SHIFT CONVERSION
CO_2
(39,300 T/D)
ACID GAS REMOVAL
SULFUR RECOVERY
SULFUR
(1805 T/D)
CLEAN – UP METHANATION
H_2 80%
REFRIGERATION
ACID GAS REMOVAL
CRYOGENIC SEPARATION
LPG (20,670 B/D)
PIPELINE GAS
(332 MM SCFD)
H_2 95%
(14,400 T/D)
SRC DISSOLVE & FILTRATION
SRC SOLVENT RECOVERY
HYDRO– CONVERSION
HYDRO– TREATING
COAL-DERIVED LIQUID
"LIGHT REFINERY LIQUID"
(100,000 B/D)
FILTER CAKE
TAR
SOLVENT REFINED COAL
(11,325 T/D)
(FOR PLANT & UTILITY FUEL)

FIGURE 1.

COG REFINERY

- Hydroconversion and Hydrotreating - These processes upgrade the solvent refined coal and light oil produced in the SRC process to the coal-derived liquid product.

- Bi-Gas Process - This is Bituminous Coal Research's coal gasification process and produces synthesis gas and methane directly from coal. This stream, after downstream purification steps, supplies the hydrogen requirements of the COG Refinery.

- Shift Conversion - This process shifts the CO in the Bi-Gas reactor effluent with steam to produce hydrogen.

- Acid Gas Absorption - Conventional hot potassium carbonate processes are employed to remove CO_2 and H_2S from both the Bi-Gas effluent and the off-gases recovered from other sections of the COG Refinery. The bulk of the CO_2, containing less than 5 ppm H_2S, is vented to the atmosphere. All the hydrogen sulfide with the rest of the CO_2 is sent to a sulfur recovery unit. A portion of this purified stream (approximately 80% H_2) is sent directly to the SRC process.

- Clean-Up Methanation - This process removes the residual CO from shift conversion to meet pipeline gas specifications.

- Cryogenic Separation - This low temperature separation is required to produce a 95% H_2 stream for hydroconversion and hydrotreating. Methane is recovered here as the pipeline gas product. LPG produced in various sections of the COG Refinery is also recovered in this section.

As seen from Figure 1, the high BTU pipeline gas consists of methane generated in the Bi-Gas and SRC processes and methane made in subsequent downstream processing steps.

The hydrotreated liquid product represents the material that will be fed to a petroleum refinery. Approximately 70% comes from hydrocracking and hydrotreating the solvent refined coal, while the remaining 30% comes from hydrotreating the light oil produced in the SRC process. The SRC process has been evaluated in the laboratory and plans are underway for a pilot plant. The design bases for the hydrocracking and hydrotreating steps have been estimated based on previous work on similar materials. The liquid product from the hydroconversion section is a 750°F end point material. The product obtained after hydrotreating is a C_5-650°F distillate with an 35° API gravity. This hydrotreated liquid product obtained from the COG Refinery represents a relatively light material for feed to a petroleum refinery. Because of these properties, this coal-derived liquid has been designated as "light refinery liquid".

The above describes how this liquid has been derived from the coal conversion processes making up the COG Refinery. The conceptual nature of the COG Refinery has been described and will be referred to later when the properties of the light refinery liquid and the way in which it will be treated in a refinery will be discussed in more detail. Before getting to that, however, it is appropriate now to discuss the approach used in the evaluation of this liquid as refinery feedstock.

APPROACH

The approach used in this study has been to determine the parity value of the light refinery liquid to a refiner compared to a standard crude. Since the objective of a refiner is to make profit, he would be willing to buy and process coal liquid as long as the properties of the coal liquid allowed him to operate as profitably as he could by processing crude oil. By determining the return on investment for a crude oil refinery, and fixing that return for a coal liquid refinery, the value of the light refinery liquid can be calculated.

In addition to comparing all crude oil and all coal liquid refineries, the evaluation also determined the effect of running mixtures of natural crude and coal liquid. This was done to see if there might be synergistic effects when processing mixtures.

LP MODEL

The analysis was performed using Chem Systems' refinery linear program (LP) computer model. The model considers the investment and operating costs associated with each of the process units which can be included in a new refinery. It makes the economic decision as to which units are to be included in the refinery, the raw material allocation among all of the process units and product blends, the operating severity of each process unit, and the optimum market slate from the refinery. The model performs an objective analysis of each problem, determining the most profitable solution available within the constraints placed on the problem.

A linear program is a technique for finding the optimum solution to a series of linear equations for which there are more variables that equations e.g., an infinite set of possible solutions. In this case, the optimum solution is the one which yields the most profitable operation for a specified set of marketing, feedstock and economic conditions. Certain variables are specified, such as capacity or feedstock, and other variables, such as operating severity levels, allocation of intermediate process streams, etc. are examined to find the solution which produces the maximum profit.

The refinery situation chosen for the evaluation is typical for the U.S. The total refinery throughput was fixed at 100,000 BPCD to avoid problems with plant size and investment factors and to match the totol coal liquid output from the COG Refinery. The process units, raw materials and product specifications considered by the refinery LP for each case are indicated in Table 1.

TABLE 1

PROCESS UNITS CONSIDERED FOR THE REFINERY

- Atmospheric Crude Distillation
- Vacuum Crude Distillation
- Naphtha Unifiner
- Catalytic Reformer
- Catalytic Cracker
- Distillate Hydrocracker
- Alkylation
- Isomerization
- Gas Oil Desulfurization
- Kerosine Desulfurization
- Hydrogen Generation

RAW MATERIAL SPECIFICATIONS

Southwest Louisiana Crude Oil	$3.50/Bbl.
Light Refinery Liquid	Price to be Determined
Normal Butane	$3.00/Bbl.
Iso Butane	$3.25/Bbl.

Total quantity of crude and coal liquid,100,000 BPCD,Mixture varied in steps from All Crude to All Light Refinery Liquid

PRODUCT SPECIFICATIONS

	Quantity	Value $/Bbl.
Gasoline Pool - 93 RON Unleaded	50,000 Min, 60,000 Max.	5.50
LPG	Unrestricted	2.83
Number 2 Heating Oil	Unrestricted	4.75
Number 6 Heating Oil	Unrestricted	3.50
Refinery Fuel Gas (FOE)	Unrestricted	3.80

The product specifications applied equally to all cases, and the reason for the limits on gasoline production was to avoid the possibility of results so widely different as to prevent meaningful comparison. The 93 RON clear specification on the gasoline pool is typical of what might be expected by 1980 when the COG Refinery would be constructed. All feed and product prices, investment, etc. are on a 1971 basis.

Before proceeding with the computer runs, certain decisions had to be made concerning the processing options available for the light refinery liquid.

PROPERTIES AND DISPOSITION OF LIGHT REFINERY LIQUID

Figure 2 shows a typical refinery configuration for feeding the coal liquid. Basically three cuts would be taken from the crude distillation unit:

- A C_5-180°F cut would go either to an isomerization unit or directly to gasoline blending.
- A 180-375°F cut would go to a catalytic reforming unit for upgrading into high octane gasoline.
- A 375-650°F cut would go either to a distillate hydrocracking unit or directly to the No. 2 fuel oil pool. The hydrocracking unit would produce a light naphtha for gasoline blending and a heavy naphtha for additional feed to the catalytic reformer. Previous work(1) on treating coal derived liquid in a refinery has indicated that hydrocracking rather than catalytic cracking should be employed to process this gas-oil cut.

Properties of each of the above cuts have been estimated and are shown in Table 2.

TABLE 2

INSPECTIONS ON LIGHT REFINERY LIQUID

		Fraction	
	C_5-180°F	180-375°F	375-650°F
Vol %	7.1	37.7	55.2
Wt. %	5.4	36.3	58.3
Gravity, °API	90	43	28
Sulfur, ppm	Nil	10	100
Nitrogen, ppm	100	200	700
Oxygen, ppm	50	200	400
P	50	20	6
O	-	-	-
N	47	65	57
A	3	15	37

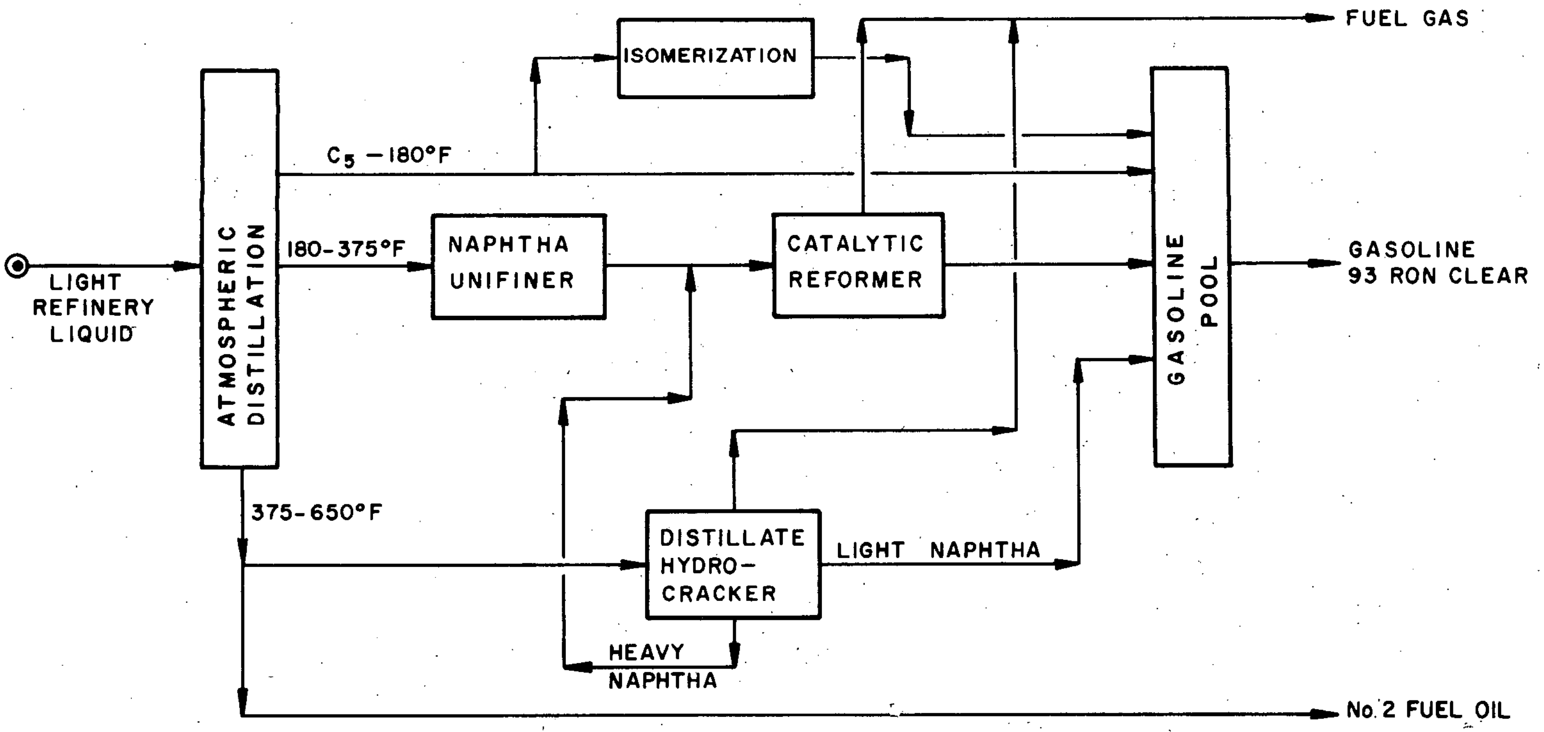
LIGHT REFINERY LIQUID
ATMOSPHERIC DISTILLATION
C_5 – 180°F
180-375°F
375-650°F
ISOMERIZATION
NAPHTHA UNIFINER
CATALYTIC REFORMER
DISTILLATE HYDRO-CRACKER
LIGHT NAPHTHA
HEAVY NAPHTHA
GASOLINE POOL
FUEL GAS
GASOLINE 93 RON CLEAR
No 2 FUEL OIL

FIGURE 2.

REFINERY PROCESSING COAL LIQUID

For comparison purposes, a typical refinery flowsheet for the all crude oil case is shown in Figure 3. As mentioned previously, cases have been considered for various mixtures of the two feeds. In those situations, the LP model has the option of selecting the optimum flowsheet configuration considering all the processing units shown in Figures 2 and 3.

DEVELOPMENT OF DATA

In order for the LP model to function, certain basic process data had to be generated, such as yields, investments and operating costs as a function of capacity for the catalytic reforming and hydrocracking units operating on the cuts from the light refinery liquid. Once developed, this data was incorporated into the basic LP data package so that the model could use it as required in determining the optimum configuration for each case considered.

Since the COG Refinery is a conceptual design, light refinery liquid has not been produced. Therefore, there is no commercial or even laboratory data available for conventional processes feeding this liquid. However, previous work has been done on similar coal-derived liquids. Chem Systems reviewed the work done by UOP on the synthetic crude produced from the bench scale research program on the Consol Synthetic Fuel Process. Additionally licensors of commercial reforming and hydrocracking processes were sent the feed properties denoted in Table 2 for their evaluation. These sources together with Chem Systems background on refinery operations have been used to estimate the necessary data for the individual processing units.

Catalytic Reforming

As seen from Table 2 the 180-375°F feed to this unit is highly naphthenic, ca. 65%. To attain high unleaded octane levels (95-102) simple dehydrogenation of the naphthenes to aromatics is sufficient. Very little cyclization or hydrocracking of paraffins would be required. This results in both a relatively simple plant and high C_5+ reformate yield. Yields, investments and operating costs have been estimated for various severity levels of reformer operation, ranging from octane numbers of 95 to 102 for the C_5+ reformate. Because the heteroatom content of the 180-375°F cut is relatively high, a pre-hydrotreating step is necessary for reforming processes that employ a noble metal catalyst. This is accomplished in the Naphtha Unifier as shown in Figure 2.

Hydrocracking

This is a conventional petroleum refining process that converts low quality middle and heavy distillates into gasoline, jet fuel and high quality middle distillates. There has been some experimental work done by UOP in a pilot scale Isomax unit utilizing a feedstock obtained from Consol's bench-scale extract hydro operations(2). The properties of Consol's feedstock are comparable to the properties of the 375-650°F cut obtained from the light refinery liquid. Their results have been used as a guide in estimating yields and operating costs for the hydrocracking unit.

The light naphtha product (C_5-180°F) from the hydrocracker has a clear octane number of approximately 82 and is sent directly to the gasoline pool. The heavy naphtha product, 180 to 375°F, has a clear octane rating of approximately 63 and therefore must be further up-graded before entering the gasoline pool. It is sent directly to the Catalytic Reformer, bypassing the Naphtha Unifier since the heteroatoms have been removed in the hydrocracking operation.

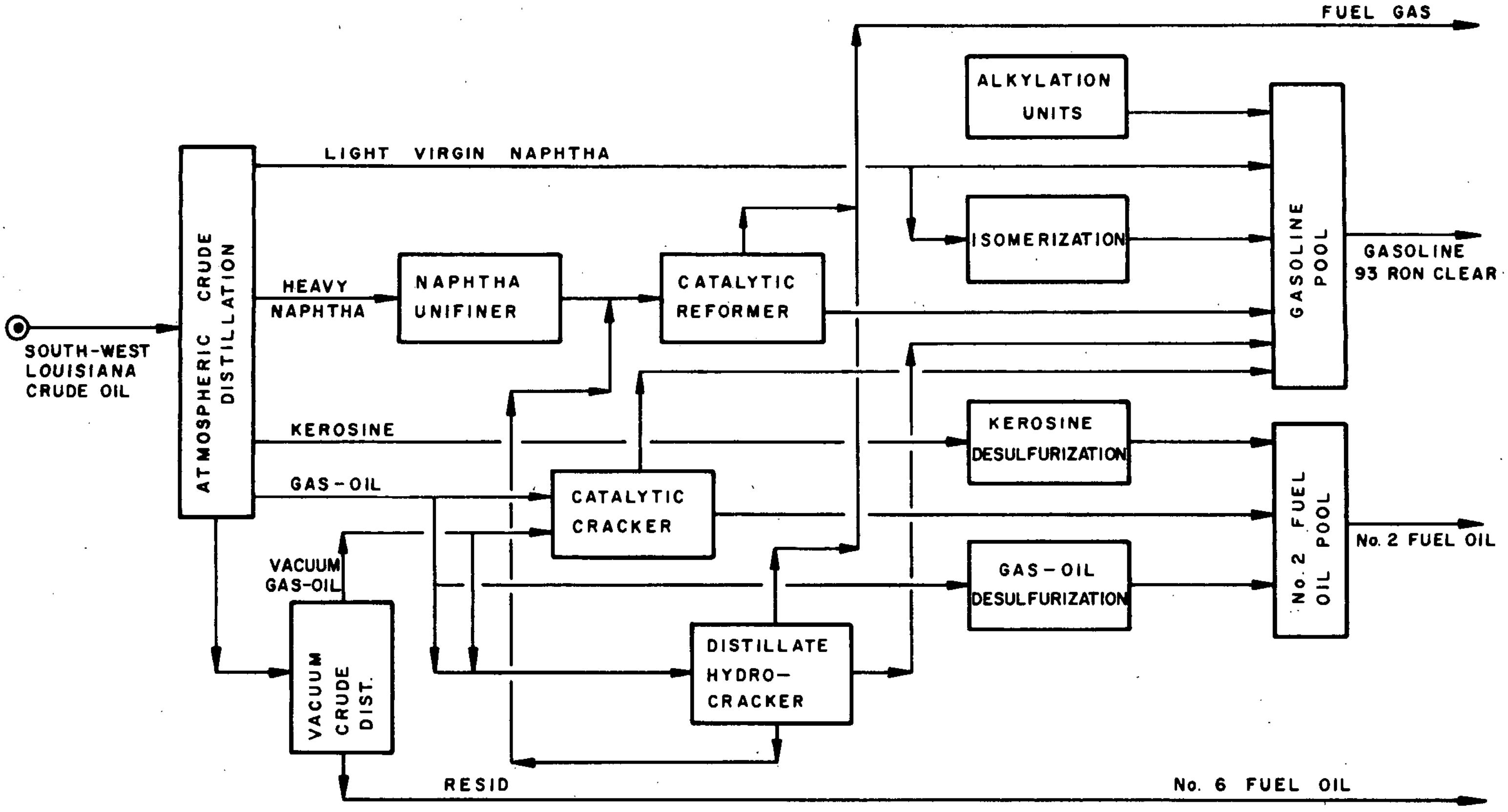
FUEL GAS
ALKYLATION UNITS
LIGHT VIRGIN NAPHTHA
ISOMERIZATION
GASOLINE POOL
GASOLINE 93 RON CLEAR
ATMOSPHERIC CRUDE DISTILLATION
HEAVY NAPHTHA
NAPHTHA UNIFINER
CATALYTIC REFORMER
SOUTH-WEST LOUISIANA CRUDE OIL
KEROSINE
KEROSINE DESULFURIZATION
GAS-OIL
CATALYTIC CRACKER
No. 2 FUEL OIL POOL
No. 2 FUEL OIL
VACUUM GAS-OIL
GAS-OIL DESULFURIZATION
VACUUM CRUDE DIST.
DISTILLATE HYDRO-CRACKER
RESID
No. 6 FUEL OIL

FIGURE 3.

REFINERY PROCESSING CRUDE OIL

CALCULATED VALUE OF COAL LIQUID

The value of the coal-derived liquid has been determined for four different ratios of coal liquid to Southwest Louisiana crude. From the basic refinery LP model the return on investment has been calculated for feeding 100% Southwest Louisiana crude at $3.50/Bbl. The value of the coal liquid then was determined which would give the same profitability as the basic crude case. Coal liquid is used to supplement Southwest Louisiana crude in percentages of 25%, 50%, 80% and 100%.

The results are summarized in Table 3. As seen, the value of the coal liquid ranges from $4.30-$5.07 per barrel with the highest value at 25% coal liquid. The value of the coal liquid as a function of feedstock ratio is shown in Figure 4. This chart indicates that the coal liquid has a higher value as a supplement to crude than when refined alone.

It can also be observed that one of the major effects of adding a coal liquid is to decrease the overall investment required for the refinery. The investment decreases from $92,100,000 for the 100% crude to only $66,100,000 for the 100% coal liquid. This reduction in investment results since there are fewer processing units required for the all coal liquid case than with the all crude oil case. Since the coal liquid has no fraction suitable for catalytic cracking, the capacity of this unit decreases to zero as the quantity of light refinery liquid is increased to 100%. The same is true for vacuum distillation since the coal liquid contains no residue. The yield of No. 6 fuel oil is decreased substantially, of course, but at the same time the more valuable No. 2 fuel oil yield is increased. Furthermore, the high octane of the coal liquid reformate means that alkylation and isomerization units are not required to satisfy the gasoline pool octane requirement as more light refinery liquid is fed to the refinery. The overall effect of these changes is to increase the overall yield of products from the refinery and to decrease both the investment and operating costs. These advantages explain why the coal liquid has a higher value than that of Southwest Louisiana crude.

SYNERGISTIC EFFECTS

The dramatic change in the value of light refinery liquid with the changing mix of crude oil and coal liquid can be explained by examining the gasoline pool. For the all crude case it is costly to the refiner to make 93 RON unleaded gasoline, and anything which relieves the difficulty is valuable to the refinery. Since the light refinery liquid is highly naphthenic, it produces a high octane reformate which is desirable for blending into the gasoline pool. Case II, (25% coal liquid) takes full advantage of this material by blending off the high octane components with reformate from the Southwest Louisiana naphtha. Since this minimizes yield losses from reforming of the straight run naphtha, the value of the coal liquid is increased proportionately. There is a definite economic advantage in converting most of the coal liquid to gasoline. With only a small amount of coal liquid in the crude mix, essentially all of it is converted to gasoline. Cases III, IV, and V fail to take full advantage of the tremendous potential of the coal liquid to produce gasoline since more and more of it must be used in No. 2 fuel oil to fulfill the product requirements. Since this is a less attractive use for it, the calculated value of the coal liquid decreases.

TABLE 3

Light Refinery Liquid Evaluation

Summary of Results - 100,000 BPCD - Feedrate

		Case I		Case II		Case III		Case IV		Case V	
Refinery Investment		$92,100,000		$82,400,000		$81,400,000		$72,200,000		$66,100,000	
	Value	MB/CD	M$/CD	MB/CD	M$/CD	MB/CD	M$/CD	MB/CD	M$/CD	MB/CD	M$/CD
Raw Materials											
Southwest Louisiana Crude	$3.50/BBL.	100.0	$350.0	75.0	$262.5	50.0	$175.0	20.0	$ 70.0	-	-
Light Refinery Liquid	calc.	-	-	25.0	126.5(1)	50.0	226.56(1)	80.0	346.56(1)	100.0	$429.65(1)
N-Butane	$3.00/BBL.	2.0	6.5	2.74	8.2	3.5	10.62	4.1	12.30	4.6	13.88
Total Raw Material Costs			356.5		397.2		412.18		428.86		443.53
Other Operating Costs			51.16		44.83		45.13		43.08		41.70
Total Production Cost			$407.66		$442.03		$457.31		$472.04		$485.23
Products											
Refinery Fuel Gas, FOE	$3.80/BBL.	4.15	15.78	4.15	15.78	3.82	14.53	1.87	7.09	0.28	1.05
LPG	2.83/BBL.	6.43	18.20	4.72	13.36	4.64	13.12	4.44	12.56	3.92	11.10
Unleaded Gasoline	5.50/BBL.	60.00	330.00	60.00	330.00	60.00	330.00	60.00	330.00	60.00	330.00
Heating Oil No. 2	4.75/BBL.	17.54	83.32	30.74	146.02	36.67	174.21	39.69	188.54	43.03	214.48
Heating Oil No. 6	3.50/BBL.	13.11	45.90	3.81	13.35	0.27	0.96	0.96	0.80	-	-
Product Revenues			$493.20		$518.51		$532.82		$538.99		$546.63
Total Production Cost			407.66		442.03		457.31		472.04		485.23
Net Income Before Taxes			$ 85.54		$ 76.48		$ 75.51		$ 66.95		$ 61.40
Value - Light Refinery Liquid	$/BBL.	-		5.07		4.54		4.33		4.30	

Notes: (1) Determined by setting the same return of investment for all cases.

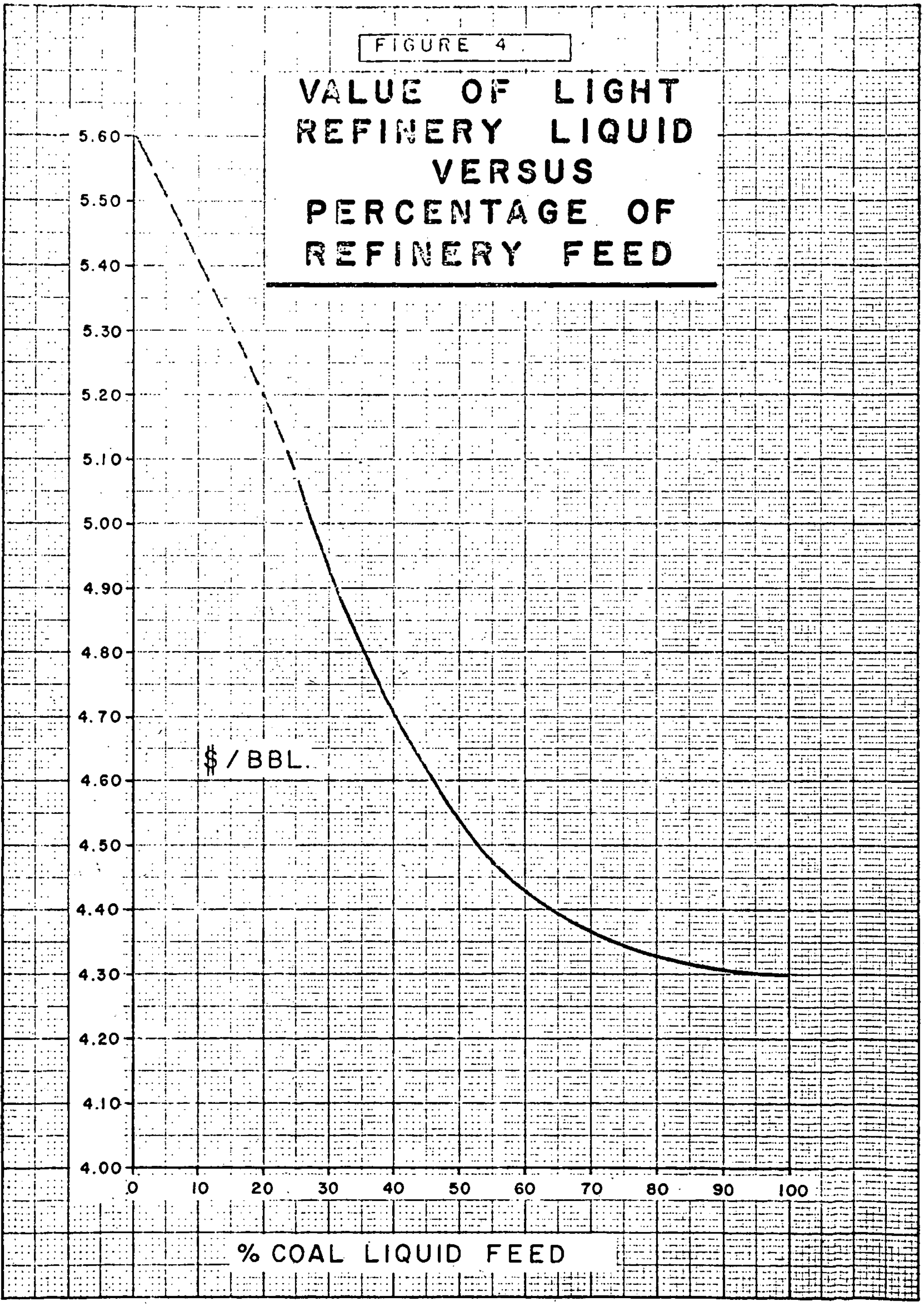

FIGURE 4

VALUE OF LIGHT REFINERY LIQUID VERSUS PERCENTAGE OF REFINERY FEED

As the net octane required from the processing of crude decreases, the value of incremental barrels of high octane blend stock also decreases. This change continues until the refinery becomes a predominantly coal liquid refinery, when the value of the coal liquid reformate and the coal liquid itself stabilizes. Due to the gasoline pool effect, the additive value of mixing coal liquid with crude can be expected to increase with an increase in the required pool octane value. The clear octane used in the study is 93 RON clear; however, values up to 95 RON clear or higher are being discussed and projected for the 1980 gasoline pool.

POTENTIAL VARIATIONS IN COAL LIQUID VALUE

The above results illustrate that coal-derived liquid can be a very valuable feedstock to a petroleum refinery even in comparison to a good quality feedstock such as Southwest Louisiana crude. Even though this study indicates that the value of the coal liquid is greatest when it is used to supplement crude oil in a petroleum refinery, it is significant that an all coal liquid refinery would save approximately $25,000,000 in investment over a conventional refinery. This would have economic advantages if the petroleum refinery were included as part of the COG Refinery.

This study was made for a typical refinery in the Kentucky-Illinois area but even a typical refinery does not adequately illustrate the full extent of benefits available by supplementing crude oil with coal liquid. Several examples are discussed below to indicate how the value of the coal liquid would be greater if different bases were used for the LP comparisons.

One obvious case is that with a refinery making more than 60% gasoline. The LP in all cases indicates that there is incentive to relax the restriction on gasoline yield. According to the LP calculations the total profitability for the refinery would be increased in all cases by increasing the gasoline yield, but the increase in profitability would be greater for the coal liquid cases.

A second example would be to permit the refinery LP model to make some chemicals rather than all fuels. It is known that there are considerable quantities of benzene, toluene and xylenes in the reformates produced from the coal liquid. The presence of significant quantities of aromatics has been confirmed by other investigations. If these materials were recovered as chemicals, the profitability of the refinery would be greater in all cases but would be increased more significantly when coal liquid was used. Thus, production of benzene, toluene and xylene from the refinery should significantly increase the calculated value of the coal liquid.

A third case would be to compare the coal liquid against a different type of crude oil. Much of the value of the coal liquid is due to the high yields of high octane reformates. This characteristic makes the coal liquid very valuable even with a high cyclic content feed material such as Southwest Louisiana crude. With a crude having a lower cyclic content in the naphtha boiling range the coal liquid would become even more valuable.

It is recognized that the calculated value of the coal liquid is somewhat dependent on the assumed value of the crude oil it replaces. For example, if the crude oil were available at no cost the calculated value of the coal liquid would be very low. On the other hand if the assumed value were higher than $3.50 per barrel the coal liquid would have a greater calculated value. Even though transportation costs were considered, the $3.50/Bbl for Southwest Louisiana crude may actually be higher for a location in the Kentucky-Illinois area. The assumed value of the crude affects the overall profitability but does not affect the refinery configuration or the schedule of products.

The assumed prices for products also have a significant effect on the calculated value of the coal liquids. Unlike changes in the crude price, however, the product prices can have a significant effect on the refinery configuration and the product slate. Sensitivity evaluation of the effect of product prices would require additional optimization studies which are beyond the intended scope of this project.

In addition to its high cyclic content, one of the most significant features of the coal-derived liquid is its low sulfur content (less than 0.01%). Since there is a shortage of low-sulfur fuels of all types, the alternate use of this material directly as a fuel rather than as a refinery feedstock should also be considered. In the Kentucky-Illinois area residual fuel of less than 1% sulfur sells for \$4.62 per barrel(3). Therefore after a simple distillation to remove light ends, the light refinery liquid could be sold directly as a fuel and should be worth at least \$4.62. It would appear that under the current assumptions a refinery could afford to pay this price for the coal liquid only if it represents less than half of the total refinery feed. Thus, it is likely that the coal liquid would be sold in some cases as a low-sulfur fuel oil. If sold as a fuel oil, however, there would really be no advantage in producing such a low-boiling material. This would allow the investment for the COG Refinery to be decreased and thereby increase its profitability. This means that a complete optimization study would have to include the entire COG Refinery. While it is an interesting possibility, it is well beyond the scope of this work. The important point here is that there would be some competition between a refinery and industrial fuel uses for the liquid produced in a COG Refinery.

SUMMARY

The results of this study clearly show that compared to \$3.50 per barrel for Southwest Louisiana crude oil, the value of the light refinery liquid produced from a COG Refinery varied from \$4.30 to \$5.07 per barrel depending upon the relative amounts of crude oil and coal liquid fed to the refinery. Even though the highest value is calculated when the coal-derived liquid is used to supplement the crude oil, it offers significant investment savings when used as the sole feedstock to the refinery. The basis selected for this study are felt to be conservative and it is probable that other equally reasonable cases would have yielded an even higher value for the light refinery liquid.

(1) PROJECT COED, U.S. Government Contract 14-01-001-498, Hydrotreating Studies - Part II - Appendix IX.

(2) Project Gasoline Pre Pilot Plant Phase I Research on CSF Process, Vol. II., Part II.

(3) Oil & Gas Journal, Vol. 69, No. 45, (Nov. 8, 1971).

Hydrogenated COED Oil

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Introduction

The COED process converts coal by fluidized-bed pyrolysis into gas, oil and char. Under Project COED, which is sponsored by the Office of Coal Research of the Department of the Interior, a 30 B/D fixed-bed catalytic hydrogenation pilot plant was constructed and operated for the hydrogenation of COED oils. This facility operates with a 36 T/D coal pyrolysis pilot plant. The Central Research and Development Department of the FMC Corporation conducts this work.

As would be expected, COED oils as produced have a high density and a low hydrogen content. In addition, they have a high concentration of heteroatoms--oxygen, nitrogen and sulfur. Hydrogenation is necessary to produce a synthetic crude oil from the COED oil to fit in with conventional refinery processing. The raw COED oil must be filtered before fixed-bed hydrogenation to remove fines. The fines content of the raw oil is reduced from about 3.0 percent to less than 0.1 percent by weight prior to hydrogenation.

The hydrogenation pilot plant was started up in May, 1971 after resolution of a number of mechanical problems. Except for recurrence of several minor mechanical problems, operation has proceeded satisfactorily.

Pilot Plant Design

The pilot plant is, in general, of conventional refinery hydrotreating design. The major equipment consists of downflow reactors with makeup and recycle hydrogen compressors and heaters. No downstream or upstream distillation equipment is included. Details were published in a project report to the Office of Coal Research[1].

One somewhat unusual feature is the use of a guard chamber-type reactor ahead of the main reactors. This was installed because it was feared that residual fine solids or the caking characteristics of the charge stock might plug the main reactors. All reactors are in series. To date no difficulty has been experienced with plugging of the guard chamber.

The design feed to this hydrotreating unit was 30 B/D of filtered COED oil with a gravity of less than zero °API. The total reactor design was for a 1.0 hourly space velocity on a weight basis. The catalyst charged to the reactors was HDS-3 catalyst produced by American Cyanamid Co. This is a 1/8-inch extrudate with 3 percent NiO and 15 percent MoO_3 on alumina. The compressors were designed to recycle enough hydrogen to produce a ratio of 18,000 scf/bbl. The maximum temperature and pressure were designed to be 950°F. at 3300 psig.

Hydrogenation Results

All of the runs reported in this study were made with a COED oil produced from the pyrolysis of a Colorado coal from the Bear Mine. This is a high-volatile B bituminous coal. The analysis of the feed oil is shown in Table I.

Demetalization

Unlike most petroleum crudes, there were very few major metallic ingredients in the COED oil. The analyses of the feed and product oil after hydrogenation are shown in Table II.

Treatment with hydrogen over a hydrogenation catalyst effectively removed iron, aluminum and silicon. Only minor effect was noted on the boron, sodium and vanadium concentrations.

Heteroatom Removal

Several long-term runs were made on the hydrogenation pilot plant. These were mainly at lower-than-design temperatures and space velocities while maintaining high recycle hydrogen rates. The results of these runs are shown in Table III.

The results shown in Table III are presented graphically in Figures 1 and 2. Because of the exothermic nature of the reaction and the spacing of the thermocouples, the reactor temperatures varied. The average throughout the beds was 650-750°F. Additional runs at higher temperatures and higher space velocities are planned and will be reported later.

As is noted on Figure 1, the heteroatom removal of sulfur, nitrogen and oxygen compounds is essentially complete at the lower space velocities and at the reactor conditions prevailing. Nitrogen was the most difficult component of the COED oil to remove on hydrotreating. Sulfur and oxygen were less difficult and almost identical, not only in the relative difficulty of removal, but also in the effect of changes in space velocity.

The effect of space velocity, other conditions nearly constant, upon API gravity of the heavy oil product is shown in Figure 2. As would be expected, the lower the space velocity, the higher the API gravity.

Because of the few runs so far from this hydrotreating pilot unit, no direct comparison can be made to previous studies[2, 3]. In general, however, the results presented here from the hydrotreating pilot unit tend to confirm the earlier bench-scale studies from the AtlanticRichfield studies. They also prove that adequate heteroatom removal in commercial units is possible at modest severities.

Product Inspections

A sample of the hydrotreated COED oil from Run H3D (maximum heteroatom removal) was distilled into several fractions. These fractions represent the conventional distillation ranges for gasoline, middle distillates, gas oil and bottoms produced in conventional petroleum refining. The approximate yields of these various cuts are shown in Table IV. The distillation curves for the raw COED oil and for the hydrotreated COED oil are presented in Figure 3.

The results of the product inspections on these various cuts are presented in Table V. Also, an ASTM distillation of the gasoline boiling-range material is presented in Figure 4.

From these petroleum-type inspections it can be readily seen that hydrotreated COED oil is a satisfactory crude oil charge to a petroleum refinery. These inspections show that these cuts can be adequately blended into conventionally produced refinery streams. The gasoline and middle distillate stocks exhibit a high gum content. This gum can be virtually eliminated by any number of conventional refinery treating processes.

The middle distillates fraction is somewhat low in gravity, as would be suspected. It would be anticipated, however, that it would be very high on a Btu per volume basis. No attempt was made to evaluate the special properties of such middle distillate fractions as jet fuel, kerosene, diesel fuel or No. 2 fuel. Color and color stability are excellent.

The higher boiling cuts also appear to be adaptable to conventional refining techniques. The gas oil fraction has a low carbon residue of 0.03 wt. percent and metals of less than 0.2 ppm nickel and vanadium. From the ultimate analysis it would appear that the residue boiling higher than 800°F. would make excellent feedstock for a carbon-black plant. From these analyses there is an indication of concentration of the nitrogen-containing molecules in the gas oil and residue fractions; no similar concentration of sulfur or oxygen is noted. The gas oil fraction should make excellent feed for either a catalytic-cracking or hydrocracking unit.

References

[1] "Char Oil Energy Development" - Project COED, Final Report; J. F. Jones, F. H. Schoemann, J. A. Hamshar, and R. T. Eddinger; Period of Performance: October 1966 - June 1971; Contract No. 14-01-0001-498.

[2] White, P. J. (ARCO Chemical Co.), Jones, J. F., and Eddinger, R.T., "To Treat and Crack Oil from Coal", Hydrocarbon Processing, 47, No. 12, pp. 97-102, December 1968.

[3] Jacobs, H. (AtlanticRichfield), Jones, J. F., and Eddinger, R. T., "Hydrogenation of COED Process Coal-Derived Oils", Ind.Eng.Chem. Process Des.Develop., 10, No. 4, October 1971.

TABLE I

Analysis of Feed Oil

Oil Source	Colorado Bear
Moisture, wt.%	0.20
Quinoline Insoluble, wt.%, dry	0.00
Ultimate Analysis, wt.%, dry	
Carbon	83.05
Hydrogen	8.35
Nitrogen	1.10
Oxygen[1]	0.35
Sulfur	7.15
Ash	0.00
°API Gravity, 60°F./60°F.	-4 to -5
Pour Point, °F.	118
Flash Point, °F.	350
Viscosity, SUS[2]	1090

[1] Oxygen determined by difference.

[2] Viscosity determined at 210°F.

TABLE II

Special Analyses of Feed and Product Oil

	Feed	Product
Run No.	-	H3D
Metals Analysis, ppm		
Iron	350	<1
Lead	<1	<1
Copper	<1	<1
Chromium	<1	<1
Aluminum	60	<1
Nickel	<1	<1
Silver	<1	<1
Tin	<1	<1
Silicon	23	<1
Boron	9	5
Sodium	6	2
Phosphorus	<100	<100
Zinc	<100	<100
Calcium	<100	<100
Barium	<100	<100
Vanadium	7	6
Magnesium	2	<1
Titanium	<1	<1
Conradson Carbon, wt.%[1]	-	0.31

[1] On a 10% ASTM distillation residue.

TABLE III

Analysis of Heavy Oil Product

Run No.[1]	H3	H4	H3D	H5
Feed Rate, lb./hr.	183.7	298.2	199.6	499.0
Space Velocity, lb. oil/hr./ lb. catalyst	0.24	0.38	0.26	0.64
Moisture, wt.%	0.31	1.42	0.00	0.90
Quinoline Insoluble, wt.%, dry	0.03	0.01	0.00	0.00
Ultimate Analysis, wt.%, dry				
Carbon	88.12	87.49	88.00	86.90
Hydrogen	11.76	10.88	11.60	10.00
Nitrogen	0.02	0.40	0.01	0.90
Sulfur	0.02	0.04	0.01	0.10
Oxygen[2]	0.08	1.19	0.38	2.10
Ash	0.00	0.00	0.00	0.00
°API Gravity, 60°F./60°F.	24.4	15.1	24.5	9.1
Pour Point, °F.	55	60	60	70
Flash Point, °F.	95	140	168	182
Viscosity, SUS[3]	46	182	44	1041
Heteroatom Removal, %				
Sulfur	94.3	88.6	97.1	71.4
Nitrogen	98.2	63.6	99.1	18.2
Oxygen	98.9	83.4	94.7	70.6

[1] All runs made at 2500 psi at temperatures between 650-750°F. with American Cyanamid AERO HDS-3 catalyst.

[2] Oxygen determined by difference.

[3] Viscosity determined at 100°F.

TABLE IV

Product Yields

	Vol. % of Hydrotreated Oil
Gasoline, IBP-400°F.	17
Middle Distillates, 400-600°F.	36
Gas Oil, 600-800°F.	31
Residual, Above 800°F.	16

TABLE V

Analyses of H3D Cuts

Run No.	H3D			
Cut, °F.	IBP-400	400-600	600-800	Residue
Moisture, wt.%	0.2	<0.2	<0.2	<0.3
Quinoline Insoluble, wt.%, dry	0.0	0.0	0.0	0.0
Ultimate Analysis, wt.%, dry				
Carbon	86.20	87.20	88.39	88.94
Hydrogen	13.74	12.40	11.51	10.89
Nitrogen	0.02	0.06	0.10	0.16
Sulfur	0.02	0.01	0.00	0.01
Oxygen[1]	0.00	0.33	0.00	0.00
Ash	0.02	0.00	0.00	0.00
°API Gravity, 60°F./60°F.	45.1	28.9	20.1	0.926[2]
Pour Point, °F.	-	-121	-31	-
Flash Point, °F.	-	148	-	-
Freezing Point, °F.	-	-	-	-
Cloud Point, °F.	-	<-60	-	-
Smoke Point	-	10	-	-
Viscosity, SUS @100°F.	<32	32.4	52.0	56.8[3]
Color	-	lighter than 1.0	-	-
Conradson Carbon, wt.%[4]	-	0.02	0.03	-
Reid Vapor Pressure, @100°F., psi	1.1	-	-	-
Copper Strip	1B	-	-	-
Gum, mg./100 ml.	63.0	2026	-	-
Octane No.	Too much gum for analysis		-	-
Aromatics	15.7	47.5	-	-
Olefins	1.4	1.4	-	-
Saturates	82.9	51.1	-	-

---

[1] Oxygen determined by difference.

[2] Specific gravity at 210°F.

[3] SUS @210°F.

[4] On a 10% ASTM distillation residue.

FIGURE I

SPACE VELOCITY VS HETEROATOM REMOVAL
(TEMP. 650-750°F, PRESSURE 2500 PSIG)

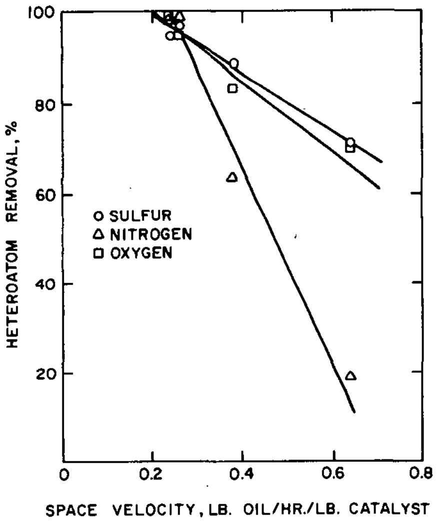


FIGURE 2

SPACE VELOCITY VS API GRAVITY
(TEMP. 650-750°F, PRESSURE 2500 PSIG)

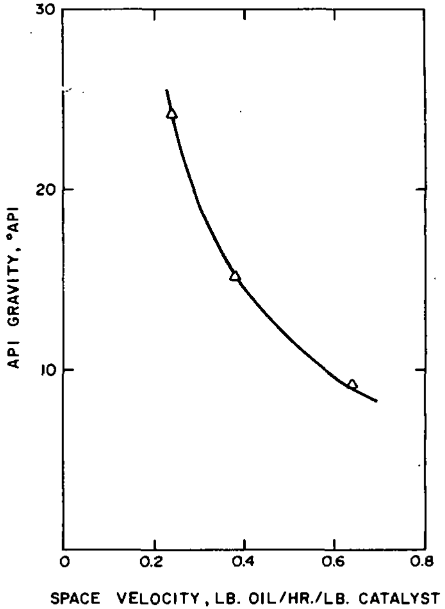


FIGURE 3

ASTM DISTILLATION
FEED OIL & H-3D HEAVY OIL PRODUCT

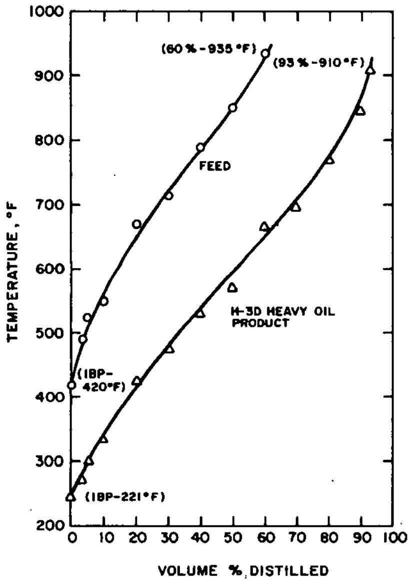
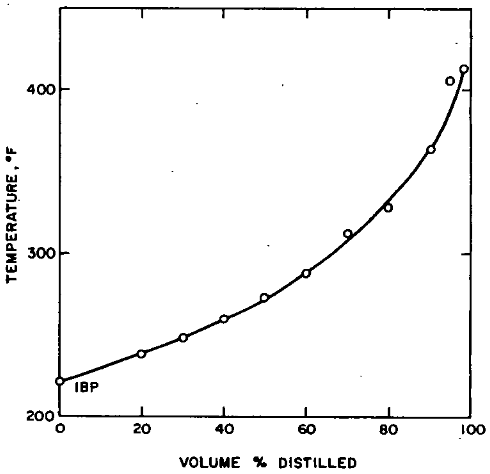


FIGURE 4

ASTM DISTILLATION
H-3D IBP-400°F CUT



QUALITY OF SYNTHETIC GASOLINE FROM COAL

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University of Utah
Salt Lake City, Utah 84112

Introduction

Gasoline can be produced from coal by a two stage process wherein coal gets converted to a synthetic crude by hydrogenation, solvent extraction, pyrolysis or carbonization in the first stage and the synthetic crude thus produced gets converted to gasoline in the second stage by hydroprocessing. The quality of gasoline depends upon the type of coal, the coal conversion process, the quality of the synthetic crude and the conditions of hydroprocessing of the crude. Coal gasolines are expected to be high in aromatic content (60-90%) when compared to petroleum gasolines since they are produced from highly aromatic (>75% aromatics) feed stocks. They, therefore, will have high octane ratings. Air quality standards may forbid the use of such high aromatic gasolines in automobiles in the very near future and it, therefore, becomes necessary to reduce the aromaticity of coal gasoline to make it acceptable. Though the coal derived gasolines are known to be high in aromatic content and octane value, not much data was published in the literature on their nature and quality. Qader and Hill[1] reported the preparation of coal naphthas by the hydrocracking of coal oils in a bench scale fixed bed system. High quality naphthas having very small quantities of sulfur, nitrogen and oxygen were obtained. The clear research octane numbers of the naphthas varied between 80 and 91. In the present investigation, data on the production of gasoline from different coal oils by hydroprocessing and the nature of the products are reported. Production of low aromatic gasolines from coal gasoline and its effect on the economics of the coal hydrogenation process are discussed. A case for the production of BTX from coal is presented.

Experimental

Low temperature tar, pyrolysis tar and solvent extracted coal were prepared in laboratory scale equipment from a high volatile bituminous coal from Utah[2]. Hydrogenation oil (coal oil) was prepared in a bench scale free fall dilute phase system[3] from the same coal. Commercial catalysts were used in the hydrorefining and hydrocracking of coal oils[4]. The evaluation of the raw materials and products was done by standard methods.

Gasoline was prepared from coal oil by hydrorefining and hydrocracking in a fixed bed reactor[1]. The aromatics were extracted from gasoline with dimethylformamide and sulfolane in laboratory mixed-Settler apparatus at room temperature. The research octane numbers were determined in the Standard Oil Company laboratories at Salt Lake City.

Results and Discussion

The nature of the coal oil depends upon the coal rank and the conversion process. Oils produced from the same coal and by different conversion processes will be different in nature. The data given in Table 1 shows that the composition of the coal oils is greatly influenced by the type of coal conversion process employed. The low temperature and pyrolysis tars are similar in nature except that the pyrolysis tar has slightly higher contents of sulfur, oxygen and residue while the low temperature tar has higher contents of nitrogen and asphaltenes. From a practical standpoint, they can be considered as similar in composition. The solvent extracted coal is very much different from the other coal oils. About 75% of the extract is composed of benzene insolubles and asphaltenes which make it a very inferior quality oil. It also has highest contents of sulfur, nitrogen, oxygen and residue. The oil obtained by coal hydrogenation is higher in quality when compared to other coal oils and this makes it a better feed stock for further processing.

The composition of the gasoline depends upon the nature of the coal oil. The data given in Table II show that the coal gasolines are high in aromatic content and the gasoline produced from coal hydrogenation oil has the highest aromaticity. The data given in Tables II and III also show that the different hydrocarbon types of these gasolines are similar in composition. The coal gasolines have very high octane ratings because of high aromaticities and a computation of octane numbers from Figure 2 shows that the clear research octane numbers of coal gasolines vary between 95 and 100. Though the high octane ratings of coal gasolines are desirable, the high aromaticities might pose problems in their future use in automobiles. Higher gasoline aromaticities will give rise to larger exhaust hydrocarbon emission which pollute the air. Though no limits in gasoline aromaticities are imposed at the present time, it is quite concievable that regulations to limit aromaticities will come into effect in the near future. It, therefore, becomes imperative to reduce the aromatic contents of coal gasolines when they are produced on a commercial scale. This can be accomplished in several ways and the most promising route seem to be by the separation of gasoline aromatics by solvent extraction. The aromatic extract can be dealkylated to produce either BTX or pure aromatics. In this work, gasoline aromatics were extracted and gasolines containing 30, 40 and 50 percent aromatics were prepared starting with a gasoline containing 76 percent aromatics. The clear research octane numbers of the gasolines decreased in straight line with a decrease in aromatic content as shown in Figure 2. The data show that gasoline containing about 50 percent aromatics will have a clear research octane number of about 83. The octane number can probably be improved to a rating of around 90 by properly adjusting the concentrations of individual aromatic components of the gasoline. The composition of the gasoline aromatics given in Table IV shows that 80 percent of the extract can be sold as BTX without further processing. The remaining 20 percent of the aromatics either can be used for blending the gasoline or can be converted to BTX by a mild treatment of dealkylation. The dealkylation of the aromatic extract produced BTX in a yield of about 95% as shown in Table V. The product contained about 62 percent benzene.

The separation of aromatics from the gasoline and the production of BTX affects the economics of the overall coal hydrogenation process. The data given in Table VI and Figure 3 indicate that the economics can be improved significantly by producing either gasoline and BTX or only BTX as the main products. The data also indicates that the coal to BTX route is the most economically attractive approach.

Acknowledgement

The work is supported by the Office of Coal Research and the University of Utah.

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TABLE I. PROPERTIES OF COAL OILS

	L.T. Carbonization	Pyrolysis	Solvent-Extraction	Hydrogenation
Benzene Insolubles, Wt.%	Nil	2.0	43.0	Nil
Asphaltenes, Wt.%	19.0	16.0	25.0	15.0
Light Oil (up to 200°C), Vol.%	5.0	7.0	3.0	18.0
Residual Oil, +370°C, Vol.%	27.0	30.0	50.0	25.0
Sulfur, Wt.%	0.82	0.98	1.15	0.64
Nitrogen, Wt.%	0.91	0.86	1.04	0.76
Oxygen, Wt.%	3.8	4.5	8.0	2.8
Tar Acids (200°-370°C Oil)	26.0	24.0	-	15.0
Hydrocarbon Analysis of Neutral Oil (200-370°C)				
Saturates	29.0	25.0		24.0
Olefins	15.0	17.0		11.0
Aromatics	56.0	58.0		65.0

TABLE II. COMPOSITION OF COAL GASOLINES

Temp: 480°C, Pressure: 2000 psi, Space Velocity: 1.0

Feed Stock:	L.T. Tar	Pyrolysis Tar	Hydrogenation Oil
Composition, Vol. %			
Saturates	30.0	26.0	13.0
Olefins	1.0	1.0	1.0
Aromatics	69.0	73.0	86.0

TABLE III. ANALYSIS OF GASOLINE SATURATES

Gasoline From:	L.T.Tar	Pyrolysis Tar	Hydrogenation Oil
Analysis, Vol.%			
N-Paraffins			
C_6	3.2	1.7	0.9
C_7	5.9	6.6	7.4
C_8	15.2	14.1	12.7
C_9	14.1	13.2	15.5
C_{10}	3.8	4.5	2.1
C_{11}	13.8	14.2	12.2
	56.0	54.3	50.8
Iso-paraffins			
C_6	3.1	1.9	2.8
C_7	11.2	8.3	10.1
C_8	10.1	12.0	16.2
C_9	9.8	13.3	10.0
	33.2	35.5	39.1
Cyclo-parrafins			
C_6	4.1	3.2	1.7
C_7	6.7	7.0	8.4
	10.8	10.2	10.1

TABLE IV: ANALYSIS OF GASOLINE AROMATICS

GASOLINE FROM:	L.T.TAR	PYROLYSIS TAR	HYDROGENATION
Analysis, Vol.%			
Benzene	33.9	30.7	40.4
Toluene	18.2	20.2	14.8
Ethylbenzene	4.5	2.8	5.5
Xylenes	25.8	27.2	19.4
Propylbenzenes	2.5	3.5	1.6
Butylbenzenes	9.0	7.0	11.3
Indanes	4.1	5.1	4.5
Unidentified	2.0	3.5	2.5

TABLE V. COMPOSITION OF THE DEALKYLATED PRODUCT

Temp: 450°C, Pressure: 1000 psi, Space Velocity: 1.0

Composition	Volume %
Benzene	62.5
Toluene	20.4
Ethylbenzene	3.0
Xylenes	9.1
Propylbenzenes	nil
Butylbenzenes	2.5
Indans	1.5
Unidentified	1.0

TABLE VI. ECONOMIC SUMMARY (COAL-GASOLINE-BTX)

Capacity: 100,000 BBL/Day Crude Oil or 46,000 TPD Coal

	Coal-Gasoline (Base Case) MM$	Coal-Gasoline (BTX: 15¢/Gal) MM$	Coal-BTX (Naphtha: 10¢/Gal) MM$
xed Capital:	418.5	440.6	440.6
orking Capital:	41.9	44.1	44.1
tal Investment	460.4	484.7	484.7
bt (65% of Total Investment):	299.2	325.1	325.1
uity (35% of Total Investment):	161.2	159.6	159.6
rect Plant Operating Cost:	134.8	136.5	137.0
venue Required:	196.0	200.8	200.8
edit for Byproducts:	53.7	142.8	87.9
oduction Cost of Product:			
oduction Cost of Gasoline:	142.3	57.2	-
oduction Cost of BTX:	-	-	112.1
Year Average Product Price:			
soline ¢/Gallon:	11.9	9.9	-
X ¢/Gallon:	-	-	13.3

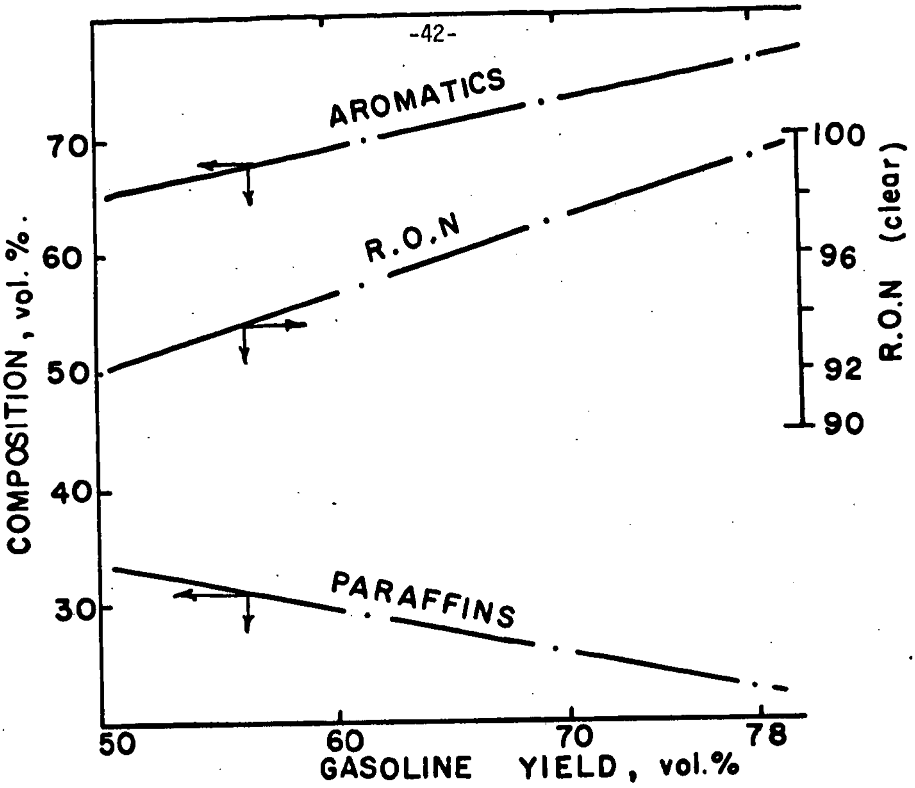

Figure 1. Yield and quality of gasoline.

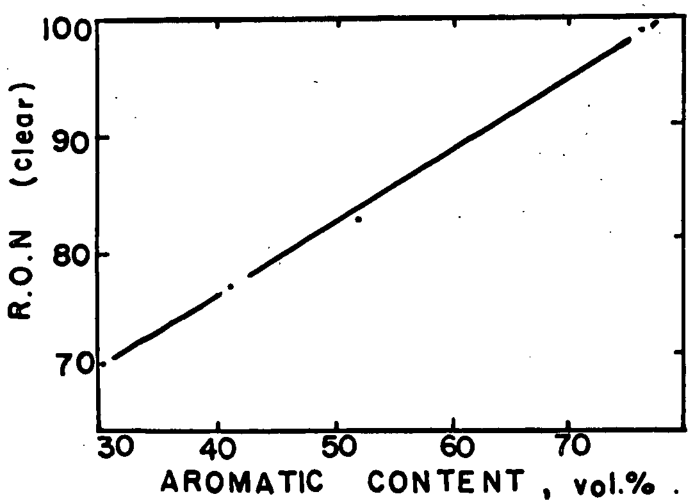

Figure 2 R.O.N and aromatic content of gasoline.

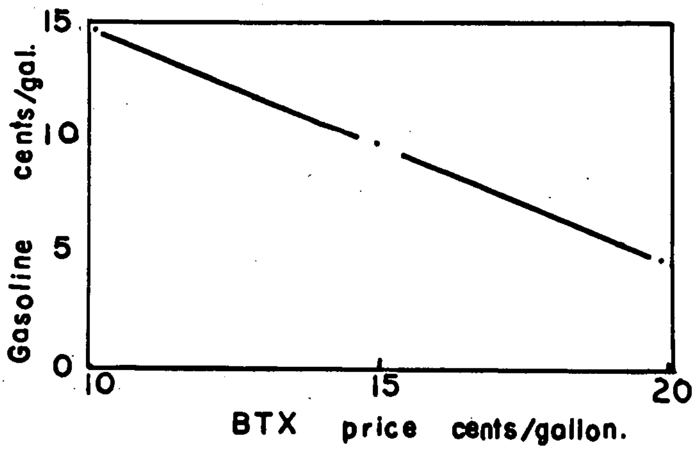

Figure 3. Variation of gasoline price with BTX price.

GASOLINE VIA THE FISCHER-TROPSCH REACTION USING THE HOT-GAS RECYCLE SYSTEM

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Introduction

One of the principal problems to be overcome in the development of a coal-to-oil process via the Fischer-Tropsch (F.T.) reaction is the removal of the highly exothermic heat of reaction of the synthesis gas (H_2+CO). The hot-gas recycle process has been developed over the past several years by the Bureau of Mines to overcome this problem.1/ In this process the heat of reaction is removed by circulating large quantities of recycle gas through a catalyst bed of high porosity. The catalyst in this experiment is a bed of parallel plates sprayed with the catalyst.

The synthesis gas sent to the F.T. reactor should contain a minimum of methane as this is considered an undesirable by-product for a coal-to-oil plant, and the sulfur content should be as low as possible (less than 0.1 ppm). The first requirement would dictate an entrained gasifier operated at very high temperature; and the second requirement can be achieved by a good purification train such as the Bureau of Mines-developed hot-carbonate process followed by a final sulfur-removal unit containing activated charcoal.

The experiment discussed in this paper used Alan Wood magnetite ore as the catalyst. The objective was to improve the product distribution over that found in an earlier test2/ and to test the use of a cheap ore as the catalyst.

Experimental Procedures and Results

Fig. 1 shows a schematic diagram of the hot-gas recycle system as developed for the synthesis of oils. The feed gas is fed to the reactor with the recycle gas. The recycle gas is a mixture of hot and cold recycle gas streams. The recycle gas temperature and volume are controlled to hold the temperature rise to about 50°C (90°F) over the reactor or the catalyst bed. The cold recycle gas stream is employed to remove product water from the recycle stream and thus control the water content of the entering gas mixture at a low enough level to prevent oxidation of the iron catalyst.

The catalyst for the present test (HGR 34) was prepared by flame-spraying powdered Alan Wood magnetite ore onto pieces of steel sheet to a thickness of about 20 mils. The sprayed steel sheets were then assembled into grids to fit into the 3-inch extra heavy steel pipe reactor. Fig. 2 shows the plates and grids. Fig. 3 shows the method of flame-spraying. The magnetite coated grid sections were dipped into a 6% aqueous solution of potassium carbonate for 5 minutes and after drying were charged to the reactor. (Concentration of K_2O on the impregnated catalyst was 0.13%.) Following reduction with hydrogen at 380-400°C, the unit was put on-stream with synthesis gas, 1.4 parts hydrogen to 1 part carbon monoxide.

The system pressure was held at 400 psig during synthesis. CO_2 was scrubbed from the cold recycle gas stream. The cold recycle gas amounted to 1.5 to 2 volumes per volumes of fresh gas. The remaining (about 18 volumes) recycle gas was used hot and unscrubbed.

Reactor Performance

Product yields of experiment HGR 34 for 1000 and 2000 space velocity operation are presented in table 1. Also presented for comparison of product distribution are yields obtained initially in experiment HGR 33 at 600 hourly space velocity operation using a flame-sprayed D3001 iron catalyst, not impregnated with alkali metal. (See analysis.) The presence of alkali metal on the sprayed Alan Wood magnetite catalyst in experiment HGR 34 is believed to be largely responsible for producing a greater proportion of gasoline range hydrocarbon than that shown initially in experiment HGR 33. While the D3001 catalyst contains K_2O, it is not as accessible as the K_2O impregnated on the surface of the Alan Wood magnetite. Also, it is believed most of the K_2O in the D3001 catalyst may have been lost in the flame-spraying.

The experimental results also indicate that the catalyst in HGR 34 was quite active. The 98.8% conversion of carbon monoxide at 1000 hourly space velocity and only slightly lower conversion at 2000 hourly space velocity attest to the high activity level of this catalyst.

TABLE 1.- Hot-gas recycle synthesis results

	Exp. No. HGR 33		Exp. No. HGR 34	
Fresh gas space velocity, vol/vol hr	600	1000	1000	2000
Total recycle in fresh feed, vol/vol	52	15.9	20.4	14.4
Reactor pressure, psig	400	400	400	400
Catalyst temperature, °C				
Average	269	325	320	325
Differential	20	50	40	50
H_2 conversion, %	73.4	90.9	90.1	83
CO conversion, %	80.6	98.8	98.2	94.4
H_2+CO conversion, %	76.4	94.4	93.4	87.5
Overall weight balance, %	93.6	90.8	87.8	96.6
Hydrocarbons recovered, lb/1000 SCF fresh gas	7.4	9.5	10.3	11.6
Hydrocarbons recovered, wt-%				
C_1+C_2	59.7	36.5	33.9	29.5
C_3	6.6	14.1	13.3	12.8
Gasoline ($C_3^=$ <204°C	31.8	43.7	48.5	53.0
Diesel oil (204°-316°C)	1.9	5.0	4.0	3.8
Fuel oil (316°-450°C)	0	0.4	0.2	0.5
Wax (>450°C)	0	0.3	0.1	0.4

Catalyst Analysis

Analyses of the Alan Wood magnetite catalyst are shown below, as is also the D3001 catalyst used in Exp. 33[2] experiment.

$Fe_{20}C_9$ is known as Hägg carbide and is considered to be a desirable form of catalyst for the F.T. reaction.[3]

	D3001	Alan Wood Magnetite	Discharged Alan Wood Magnetite (Section 4)
Iron (Fe)	66.8%	66.1	85.2 (Fe_2O_3)
Chromium oxide (Cr_2O_2)	0.8	0.08	0.0
Magnesium oxide (MgO)	4.6	0.09	0.04
Manganese oxide (Mn_3O_4)	0.05	0.04	0.02
Potassium oxide (K_2O)	0.61	0.13	0.10
Silicon dioxide (SiO_2)	0.62	5.4	0.50
Titanium oxide (TiO_2)			0.5

The x-ray analysis of the HGR 34 catalyst taken from the 12 sections after discharge are shown below:

Section	Phase 1	Phase 2	Phase 3
1 (bottom - gas inlet)	Fe_3O_4	$Fe_{20}C_9$	
2	Fe_3O_4	$Fe_{20}C_9$	
3	Fe_3O_4	αFe	
4	Fe_3O_4	αFe	
5	Fe_3O_4	$Fe_{20}C_9$	
6	Fe_3O_4	$Fe_{20}C_9$	
7	Fe_3O_4	$Fe_{20}C_9$	
8	Fe_3O_4	$Fe_{20}C_9$	
9	Fe_3O_4	αFe	γFe_2O_3
10	Fe_3O_4	αFe	γFe_2O_3
11	Fe_3O_4	αFe	
12 (top - gas outlet)	Fe_3O_4	αFe	γFe_2O_3

The experiment was ended voluntarily after 540 hours of synthesis, and the plates were removed and kept under inert gas. The fourth plate from the bottom showed blistering or separation of the coating from the steel sheet although the coating was intact until the samples were taken. The lower eight assemblies were clean but the top four contained loose carbon and loose coating. The top two grids were of stainless steel and lost all their coating; the other 10 were of carbon steel. The use of stainless steel plates is apparently not desirable owing to the difficulty of retaining the Alan Wood magnetite coating. The flow of gas is upward, and the hottest temperature (about 350°C) is at the top where the carbon is formed. It is possible that 350°C is too high a temperature to operate an iron catalyst though this conclusion depends on the CO partial pressure that the catalyst actually "sees".

Oil and Water Analyses

The oil analyses of the light and heavy oils showed Bromine numbers between 30 and 40 for the light oil and between 8 and 10 for the heavy oil indicating that the olefinic content of the oil is a maximum of about 22%. Most of the product oil is light oil as shown in Table 1. The oil was slightly acidic indicating production of organic acids, principally acetic acid.

The water analysis averaged about 94% water, the balance being alcohols; the major alcohol was ethanol with lesser amounts of methanol, propanols, and butanols.

Gas Analysis

A typical tail gas analysis is:

H_2	44.3%	C_2H_4	0.3%	C_4H_{10}	1.3%
CO	9.7	C_2H_6	6.5	C_5H_{10}	0.6
N_2	0.9	C_3H_6	0.9	C_5H_{10}	0.5
CO_2	7.9	C_3H_8	4.5	C_6H_{12}	0.2
CH_4	21.4	C_4H_8	1.1	C_6H_{14}	0.1

Note the lower concentration of the olefins; this is assumed to be due to the formation of alcohols and acids.

The C_3H_6 (but not C_3H_8) and heavier hydrocarbons are considered in the gasoline fraction. Attempts were made in earlier experiments[2] to pass the tail gas through a second reactor containing nickel methanation catalyst to form a high-Btu gas and thus have 2 saleable products, the oils and the high-Btu gas. However, the nickel catalyst became plugged with carbon owing to the low H_2/CO ratio of 1.9 and decomposition of the higher hydrocarbons.

It is believed that a satisfactory high-Btu gas could be made from the gas analyzed if the higher hydrocarbons were removed as the H_2/CO ratio is above 3/1. This would be the desirable method of operation since the upgrading of the tail gas increases its value.

Conclusions

The test to make a gasoline product by the Fischer-Tropsch reaction using sprayed plates of magnetite ore was successful. The make of gasoline was about 60% of the hydrocarbon production. The catalyst held up well under 540 hours of synthesis, and the test was ended voluntarily. The hourly space velocity for the latter part of the experiment was 2000. This showed the catalyst had very good activity.

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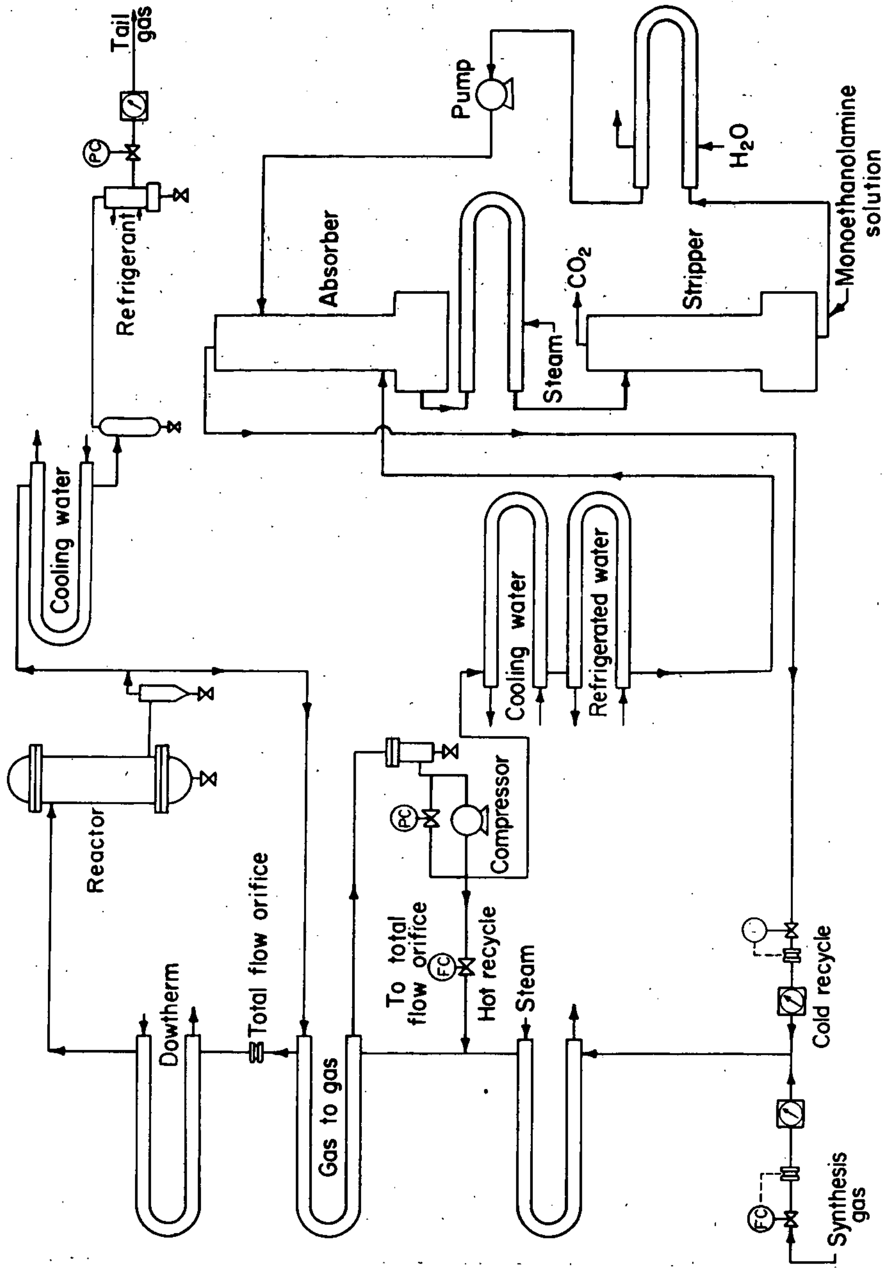
Tail gas
PC
Refrigerant
Cooling water
Pump
Absorber
Steam
CO_2
Stripper
H_2O
Monoethanolamine solution
Reactor
Total flow orifice
Dowtherm
Gas to gas
Cooling water
Refrigerated water
PC
Compressor
To total flow orifice
FC
Hot recycle
Steam
Cold recycle
FC
Synthesis gas

Figure 1. Hot-Gas-Recycle Flowsheet for Production of Gasoline.

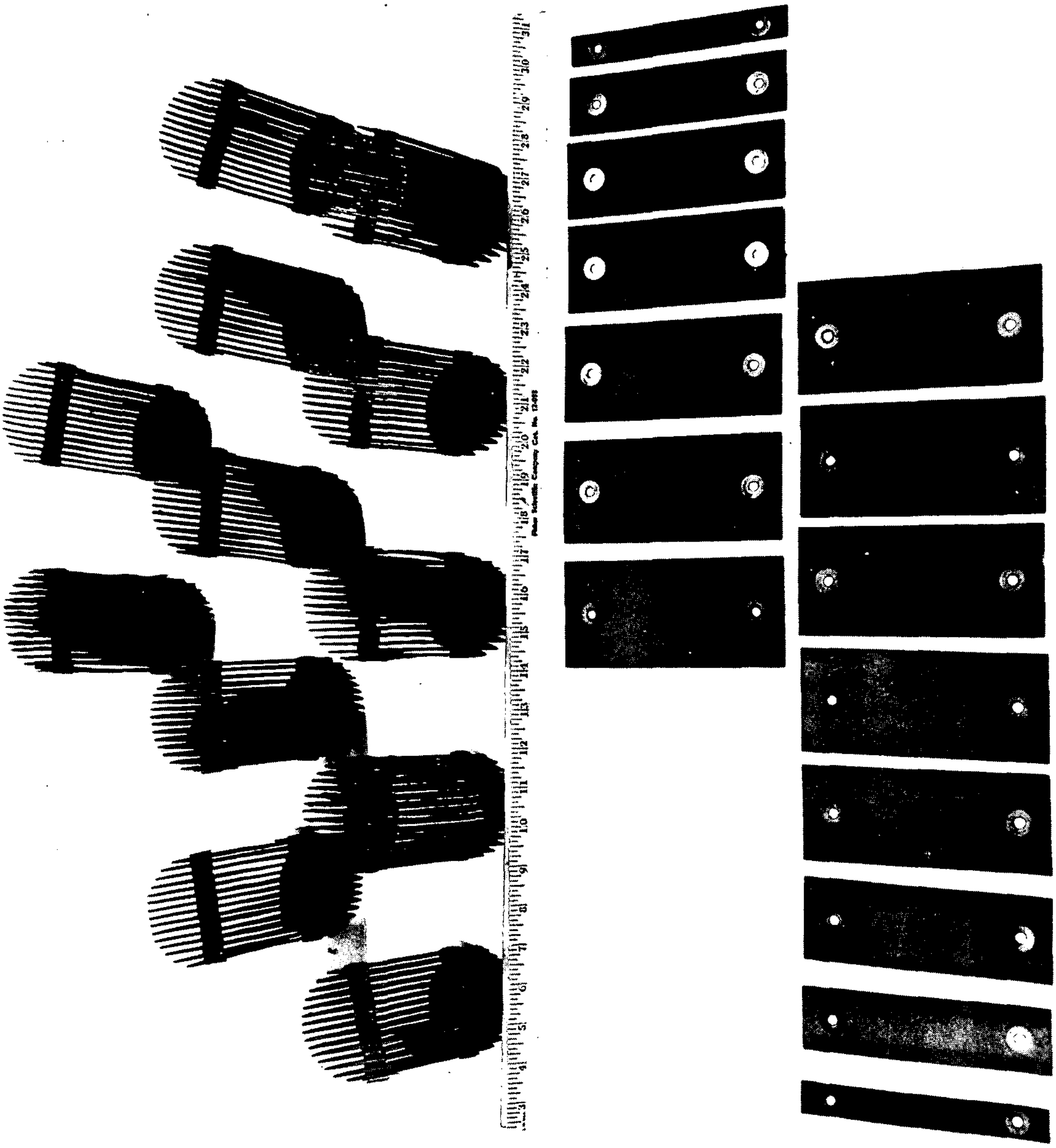

Figure 2. Plates and Grid Assemblies Used in the Production of Gasoline.

Figure 3. Apparatus Used in Thermal Spraying.

QUALITY REQUIREMENTS FOR SNG

George Long

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Substitute natural gas (SNG) produced from liquid or solid fuels will become a major factor in supplementing our natural gas supply during this decade. To date, six plants to produce 1.6 billion cubic feet per day of SNG from liquid fuels and two plants to produce 500 million cubic feet per day of SNG from coal have been announced. Although this half a trillion cubic feet per year of SNG is minuscule in relation to the 23 trillion cubic feet of natural gas distributed last year, some consideration must be given to the quality requirements if this SNG is to be satisfactory to the domestic gas industry.

To be a satisfactory supplement, SNG must be completely interchangeable with natural gas. One way to assure complete interchangeability is to synthesize a product having the same composition as natural gas. In nearly all cases this means synthesizing a product consisting of over 85% methane.

In the processes under consideration for producing SNG from liquid or solid fuels, the product gas must undergo a catalytic methanation step to achieve methane contents approaching 85% methane. This operation adds cost to the SNG, and it may not be to the best interest of the consumer or the gas industry to synthesize a high methane SNG if other compositions are satisfactory. This paper will show that a wide range of gas compositions can be satisfactorily substituted for natural gas.

In 1965, Grumer and Harris[1] performed a study of the interchangeability of methane-hydrogen mixtures with natural gas. They found that complete identity between the substitute and natural product is not necessary. Methane-hydrogen mixtures having between 25 to 37% hydrogen can be tolerated in the sendout gas.

The American Gas Association[2] has developed empirical indices to compute the interchangeability of various gas mixtures used for peaking. This investigation studied the effect of supplemental gases such as coke oven gas, producer gas, carburetted water gas,and hydrocarbon-air mixtures, in admixture with natural gas on combustion characteristics of appliances.

In order to properly assess the interchangeability factors, one must consider the use of natural gas and the effect of compositional change on the customers involved. Table I shows the gas demand in 1970 as to class of service. Nearly 21-1/2 trillion cubic feet of natural gas were distributed in 1970. Thirty-two percent was sold to residential and commercial customers. All of these seven trillion cubic feet were used for energy in the form of heat. The industrial category consumed 27.7% of the total in various applications: as heat, controlled atmosphere, chemical feedstock, and others. The electric utility consumed 18.3% of the gas as fuel in power generation. The interruptible category of three trillion cubic feet was probably used as heat because it is an economical form of heat for the large volume customer. The other category includes company uses, transmission mainline fuel, and other sales not otherwise classified. Over two thirds of all the gas distributed is used in combustion.

This is not the whole story. Table II shows the gas consumers broken down into type of customer. The residential and commercial customers constitute 99-1/2% of the total number of customers, leaving only 0.6%. These 249,000 customers, including industrial, electric utility, and interruptibles, consume over 60% of the natural gas. In terms of sheer numbers, over 41 million customers use natural gas as fuel and if the interchangeability requirements are designed to satisfy these users, the balance can be handled on an individual basis if needed. Therefore, this paper will address itself to quality requirements of SNG when used as a heat source in combustion devices used in residential and most commercial and industrial applications.

The properties of SNG must be such that there is minimum effect on performance of gas appliances when it is substituted for natural gas. This means that the SNG should give similar heat inputs, good flame stability, and complete combustion without adjustment of the appliance. Table III shows the interchangeability factors used for assessing substitutibility.

In a gas appliance having a fixed orifice, the flow of gaseous energy or heat input through the orifice at constant pressure varies directly as the heating value, h, of the gas and inversely at the square root of the specific gravity, d. This relationship is referred to as the Wobbe number. Empirically, if the Wobbe number of the two gases is within 10%, the gases are interchangeable, providing othe factors do not adversely affect flame characteristics. The Wobbe number is useful for a cursory examination of the interchangeability of two gases because of its simplicity. Alone, the Wobbe number does not give a definitive answer to interchangeability. The British Gas Council[5] has developed a combustion diagram which relates the Wobbe number to a flame speed factor. In this relationship, the Wobbe number must not fall below 1202 to ensure satisfactory heat input to an appliance. For SNG with a heating value of 1000 BTU/CF, the Wobbe number should be in the range of 1335 ± 5% and a flame speed as low as possible.

To assess the flame characteristics of SNG burned in an appliance adjusted for burning natural gas, the interchangeability indices developed by the A.G.A. Labo tories[2] are believed to be more useful because they take into account the composition of the substitute gas.

Three empirical indices were developed to compare flame characteristics. These are, I_L, the lifting index, I_F, the flashback index, and I_Y, the yellow-tip index. These indices, valid for gases having a heating value greater than 800 BTU/C will predict if the substitute gas will cause flame lifting, yellow-tipping, or flas back. I will not discuss the parameters entering into each index; these are discuss in the bulletin. In Table III it will suffice to show the range of values desired.

In addition to these computations on SNG substitutibility, actual applianc combustion tests were made to confirm the results. A wide variety of burners was used to ensure that most combustion appliances were covered.

GAS COMPOSITIONS CONSIDERED AND TESTED

Five different SNG gas compositions were considered for their interchangeability with natural gas - four compositions from naphtha gasification and one from coal gasification. The names of the processes for SNG production are identified in this paper to depict actual situations and to facilitate understanding and do not imply process endorsement by the author.

1. SNG from Single-Stage Gasification

The first gas composition for interchangeability considerations was that product gas from a single-state catalytic gasification of naphtha with steam. Figur 1 shows the product composition from the British Gas Council process after CO_2 remov The gas composition consists of 80% methane with 17.4% hydrogen. It has a heating value of 869 BTU/CF and a specific gravity of 0.493. This gas is considered for interchange with a natural gas of 1030 BTU/CF heating value and 0.587 gravity.

The Wobbe number of the SNG is 1238, and that of the natural gas is 1343. The ratio of the Wobbe number, W_n/W_s, is 1.087; i.e., the Wobbe numbers are within 8% of each other. This means that the heat input rate through a fixed orifice is within acceptable limits and the gases are interchangeable, providing other factors do not adversely affect flame characteristics.

The interchangeability indices are well within the acceptable limits for lifting, flashback, and yellow-tipping.

Combustion tests show this particular gas to be completely interchangeable with the natural gas.

2. Above SNG Enriched with Ethane

Since some utilities may have to meet certain heating value requirements, this SNG gas was enriched with ethane to 1030 BTU/CF. Figure 2 shows the pertinent data. The heating value was adjusted with ethane to the same as the natural gas, 1030 BTU/CF. The specific gravities of 0.589 for the SNG and 0.587 for the natural gas were nearly identical. The Wobbe number for SNG, 1341, is within 0.1% of the 1343 Wobbe number of the natural gas.

The interchangeability indices show that all are within the preferred range except of I_Y, yellow-tipping, which is outside the limits. The I_Y was computed to be 0.943 whereas the preferred value should exceed 1.0. This would indicate possible yellow-tipping, and combustion tests confirmed a slight tendency to yellow-tip. The amount, however, was not considered objectionable and we consider the gas interchangeable.

3. SNG After Two-Stage Gasification and CO_2 Removal

In the British Gas Council process for SNG from naphtha, the methane content can be increased by adding a hydrogasification step. Figure 3 shows this gas composition after CO_2 removal. The heating value is 934 BTU/CF compared to 869 BTU/CF for the single-stage treatment. The Wobbe numbers are within 6% which indicate the flow rate should be satisfactory. The interchangeability indices are within the preferred ranges. Combustion tests confirmed that this gas is completely interchangeable with the natural gas.

4. Above SNG Enriched with Ethane

The SNG from two-stage gasification was enriched with ethane to 1030 BTU/CF to bring the heating value to that of the natural gas. Figure 4 shows the pertinent data. Note that the Wobbe numbers are within 1%, indicating satisfactory heat input flow rate through a fixed orifice. You will recall that 10% is acceptable.

The interchangeability indices show that I_L and I_F are within the preferred limits. The yellow-tipping index, I_Y, is outside the preferred limit of 1.0 or above. This means that the gas may show yellow-tipping and indeed this was confirmed by combustion tests. However, the amount of yellow-tipping was not objectionable and we consider the gas interchangeable.

5. SNG from Coal Gasification

The last case considered was SNG from coal gasification. Figure 5 shows the gas composition expected from the HYGAS process under development at the Institute of Gas Technology. This SNG consists predominately of methane, 93%, and about 6-1/2% hydrogen. Its heating value of 968 BTU/CF and specific gravity of 0.545 yields a Wobbe number of 1312. This is within 2.4% of the natural gas, well inside the 10% acceptable limit.

The interchangeability indices show that I_L, the lifting index, is 1.0 compared to the preferred value of less than 1.0. The other indices are within the preferred range.

Combustion tests showed this SNG to have a slight tendency to lift, confirming the I_L indication. However, the lifting was so slight that we considered the gas completely interchangeable.

CONCLUSIONS

A wide range of gas compositions produced from liquid and solid fuels was found to be interchangeable with natural gas. SNG having a heating value ranging from 869 BTU/CF to 1030 BTU/CF was shown to be interchangeable with a 1030 BTU/CF high methane natural gas.

The A.G.A. interchangeability indices plus the Wobbe number can predict substitutibility. Combustion tests using a wide variety of burners confirmed the validity of these empirical indices.

REFERENCES

[1] Grumer, Joseph, and Harris, Margaret E., *Exchangeability of Synthetic Gases from Solid Fuels with Pipe Line Natural Gas*, Bureau of Mines Report of Investigation 6629, U.S. Department of the Interior, 1965.

[2] Research Bulletin 36, *Interchangeability of Other Fuel Gases with Natural Gas*, American Gas Association, 1952.

[3] *Future Gas Requirements of the United States, Volume 4, October, 1971*, Future Requirements Agency, Denver Research Institute, University of Denver, Denver, Colorado.

[4] *Gas Utility and Pipeline Industry Projections*, Department of Statistics, American Gas Association, Inc., Washington, D. C.

[5] Davies, H. S., Lacey, J. A., and Thompson, B. H., *Process for the Manufacture of Natural-Gas Substitutes*, Research Communication GC 155, The Gas Council, London, (1968).

TABLE I

U.S. Gas Requirement - 1970

	Trillions of Cubic Feet	% of Total
Residential	4.94	23.1
Commercial	1.96	9.1
Industrial	5.94	27.7
Electric utility	3.92	18.3
Interruptible	3.09	14.4
Other	1.58	7.4
Total	21.43	100.0

Source: *Future Gas Requirements, October, 1971.*[3]

TABLE II

Gas Customers - 1970

	Thousands	% of Total
Residential	38,303	91.8
Commercial	3,158	7.6
Industrial and others	249	.6
Total	41,710	100.0

Source: American Gas Association, Inc.,
Department of Statistics.[4]

TABLE III

Interchangeability Factors

$$\text{Wobbe No.} = \frac{\text{heating value}}{\sqrt{\text{specific gravity}}} = \frac{h}{\sqrt{d}}$$

I_L = under 1.0; above 1.06

I_F = under 1.18; above 1.2

I_Y = above 1.0; under 0.8

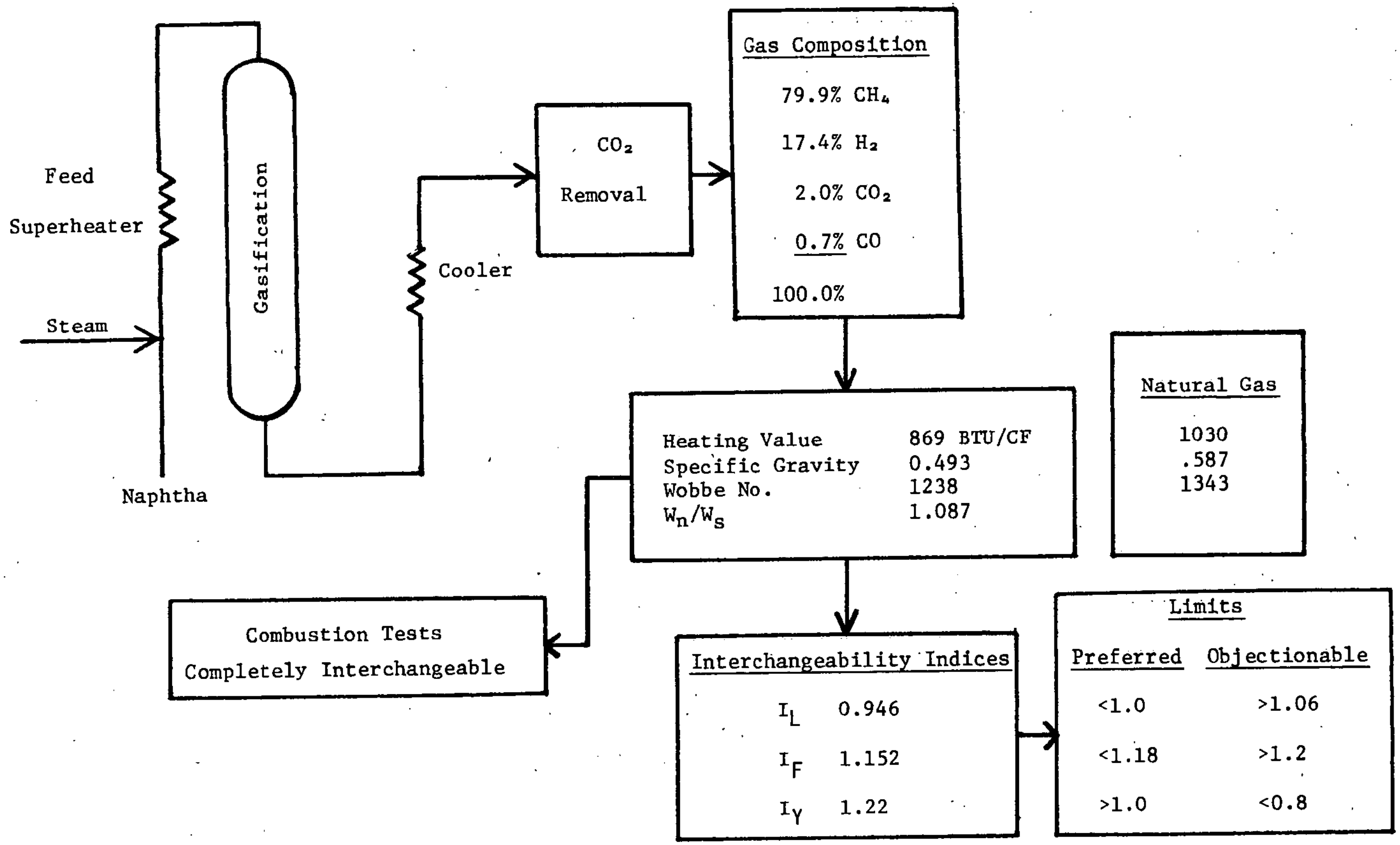
Feed
Superheater
Steam
Naphtha
Gasification
Cooler
CO₂ Removal
Gas Composition
79.9% CH₄
17.4% H₂
2.0% CO₂
0.7% CO
100.0%
Heating Value 869 BTU/CF
Specific Gravity 0.493
Wobbe No. 1238
Wn/Ws 1.087
Natural Gas
1030
.587
1343
Combustion Tests
Completely Interchangeable
Interchangeability Indices
IL 0.946
IF 1.152
IY 1.22
Limits
Preferred Objectionable
<1.0 >1.06
<1.18 >1.2
>1.0 <0.8

FIGURE 1: SNG AFTER SINGLE-STAGE GASIFICATION AND CO_2 REMOVAL

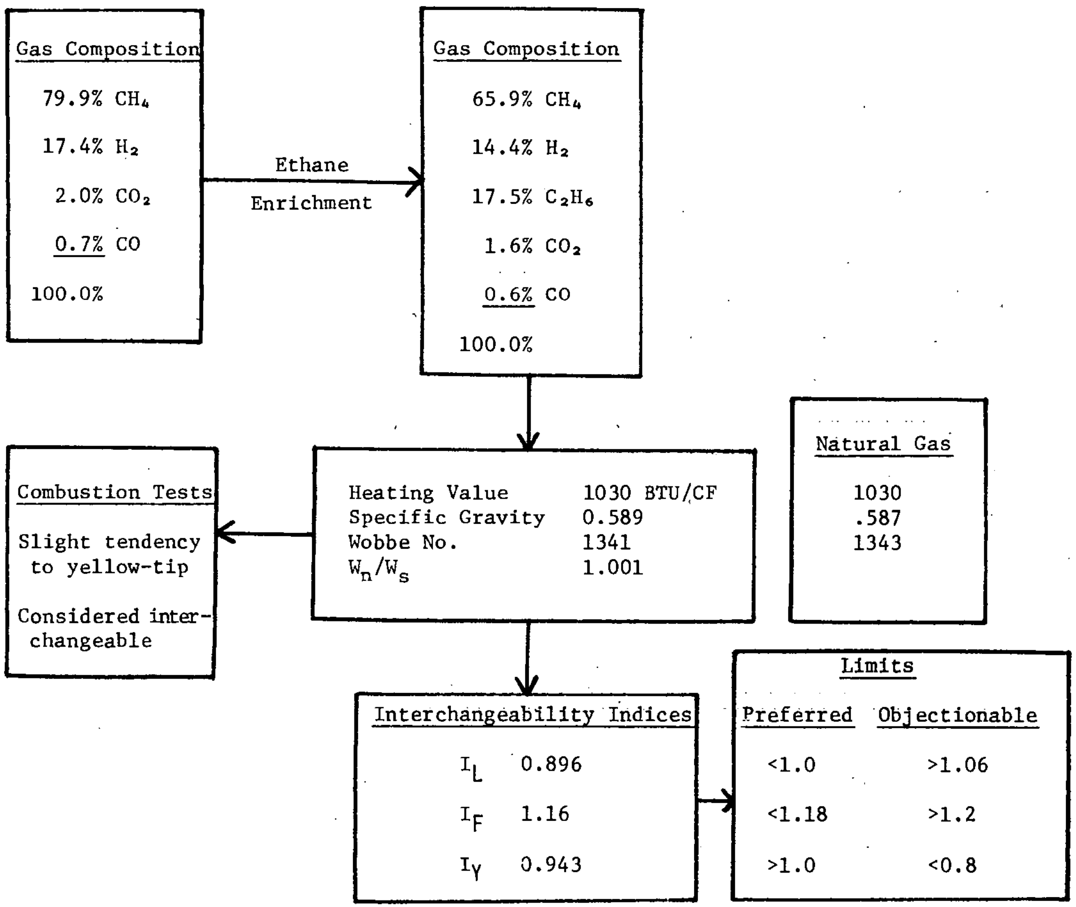
Gas Composition
79.9% CH₄
17.4% H₂
2.0% CO₂
0.7% CO
100.0%
Ethane
Enrichment
Gas Composition
65.9% CH₄
14.4% H₂
17.5% C₂H₆
1.6% CO₂
0.6% CO
100.0%
Heating Value 1030 BTU/CF
Specific Gravity 0.589
Wobbe No. 1341
Wn/Ws 1.001
Natural Gas
1030
.587
1343
Combustion Tests
Slight tendency to yellow-tip
Considered interchangeable
Interchangeability Indices
IL 0.896
IF 1.16
IY 0.943
Limits
Preferred Objectionable
<1.0 >1.06
<1.18 >1.2
>1.0 <0.8

FIGURE 2: SNG ENRICHMENT WITH ETHANE

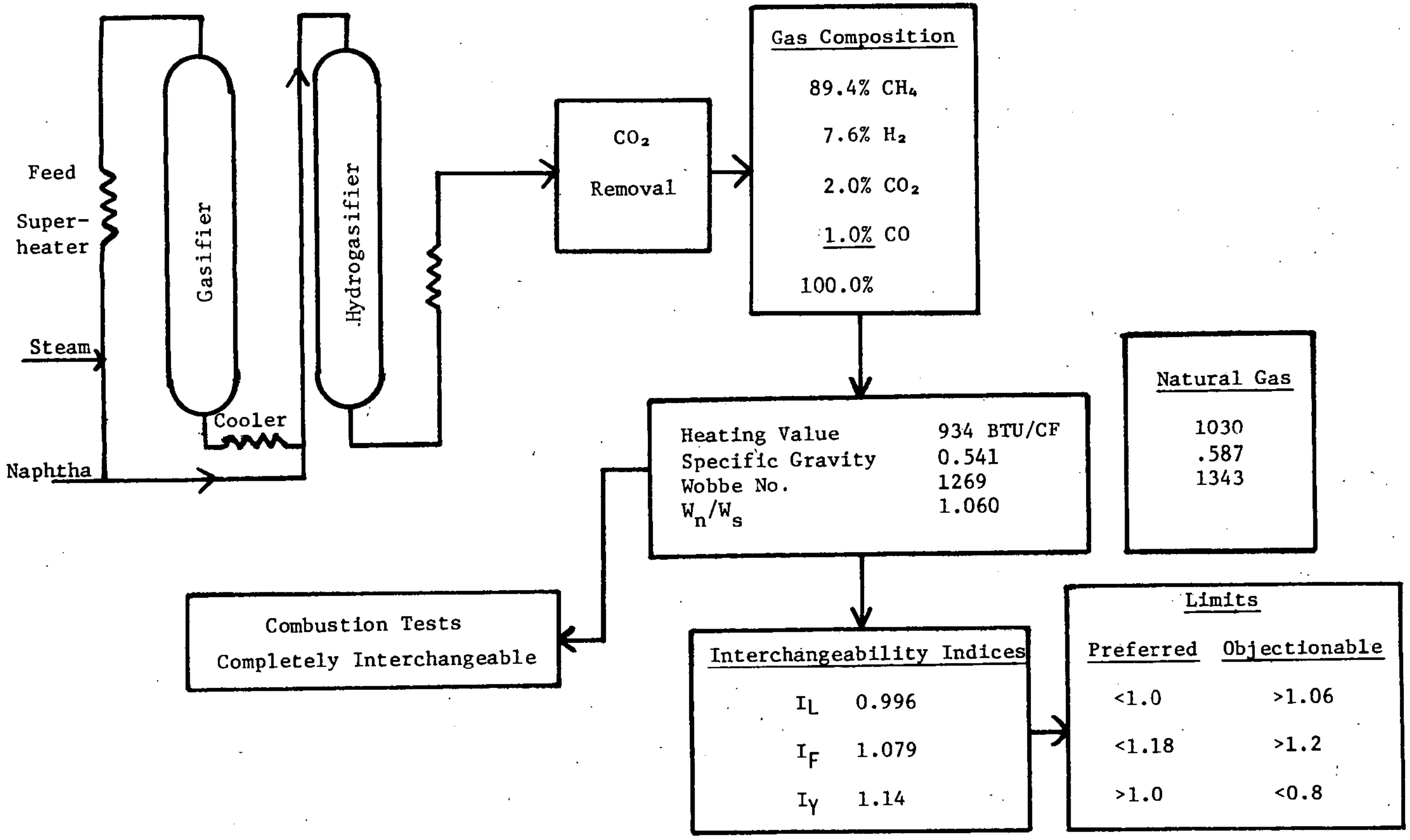
Feed
Super-heater
Steam
Naphtha
Gasifier
Cooler
Hydrogasifier
CO₂ Removal
Gas Composition
89.4% CH₄
7.6% H₂
2.0% CO₂
1.0% CO
100.0%
Heating Value
Specific Gravity
Wobbe No.
Wn/Ws
934 BTU/CF
0.541
1269
1.060
Natural Gas
1030
.587
1343
Combustion Tests
Completely Interchangeable
Interchangeability Indices
IL 0.996
IF 1.079
IY 1.14
Limits
Preferred
Objectionable
<1.0 >1.06
<1.18 >1.2
>1.0 <0.8

FIGURE 3: SNG AFTER TWO-STAGE GASIFICATION AND CO_2 REMOVAL

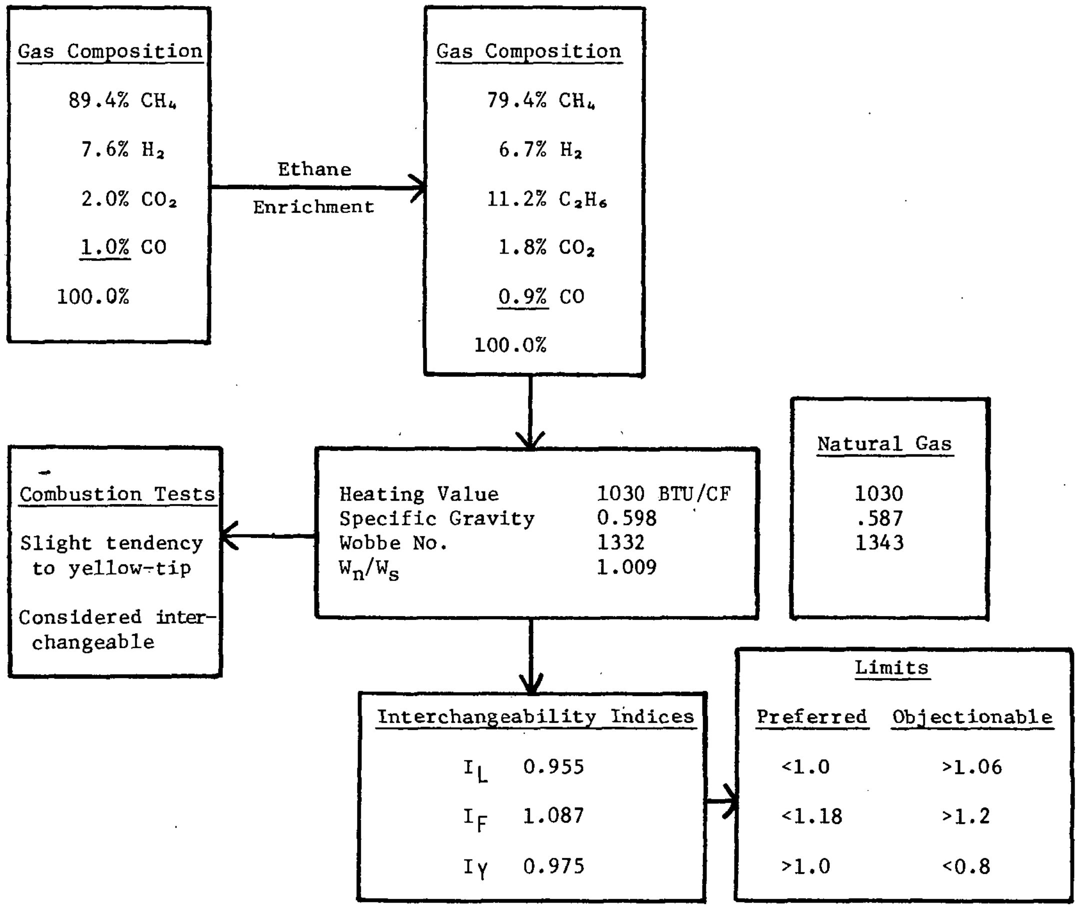
Gas Composition
89.4% CH_4
7.6% H_2
2.0% CO_2
1.0% CO
100.0%
Ethane
Enrichment
Gas Composition
79.4% CH_4
6.7% H_2
11.2% C_2H_6
1.8% CO_2
0.9% CO
100.0%
Combustion Tests
Slight tendency to yellow-tip
Considered interchangeable
Heating Value 1030 BTU/CF
Specific Gravity 0.598
Wobbe No. 1332
W_n/W_s 1.009
Natural Gas
1030
.587
1343
Interchangeability Indices
I_L 0.955
I_F 1.087
I_Y 0.975
Limits
Preferred
Objectionable
<1.0
>1.06
<1.18
>1.2
>1.0
<0.8

FIGURE 4: SNG AFTER ENRICHMENT WITH ETHANE

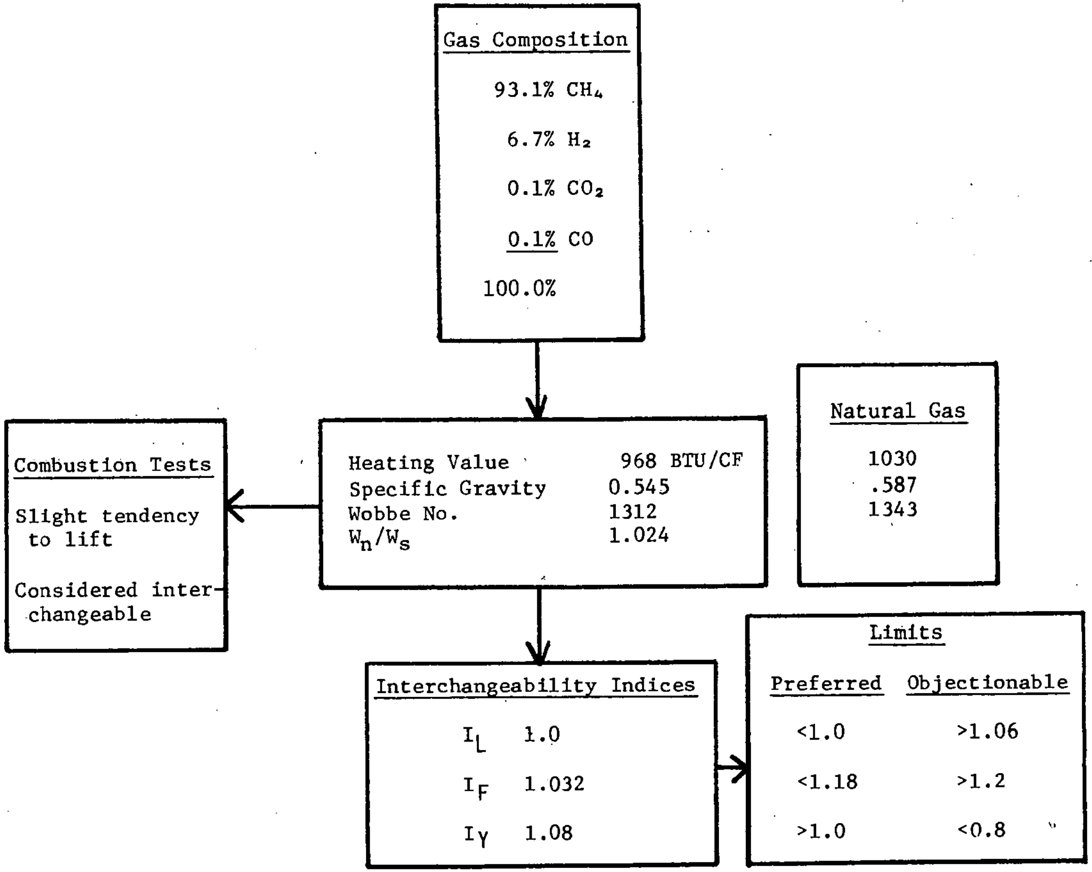
Gas Composition
93.1% CH_4
6.7% H_2
0.1% CO_2
0.1% CO
100.0%
Heating Value 968 BTU/CF
Specific Gravity 0.545
Wobbe No. 1312
W_n/W_s 1.024
Natural Gas
1030
.587
1343
Combustion Tests
Slight tendency to lift
Considered interchangeable
Interchangeability Indices
I_L 1.0
I_F 1.032
I_Y 1.08
Limits
Preferred
Objectionable
<1.0
>1.06
<1.18
>1.2
>1.0
<0.8

FIGURE 5: SNG FROM COAL GASIFICATION

OIL SHALE AS A POTENTIAL ENERGY SOURCE

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INTRODUCTION

Although the physical exhaustion of petroleum resources appears to be many years away, the increasing demand for petroleum has led to concern for adequately meeting future demand. The conversion of oil shale to a synthetic crude oil, which can be accomplished by various systems under consideration, is one of the several alternative ways to supplement petroleum requirements.

An oil shale processing complex consisting of three mines, three retorting plants, and a prerefinery has been proposed for the production of 100,000 barrels per calendar day of semirefined oil. Included are the equipment and installation for mining and retorting in the Roan Creek area in Colorado and the pipelining of the gas and crude oil to the prerefinery in DeBeque, Colo. In addition, the cost of chemicals and catalyst, interest during construction (plants), interest during development (mine), startup expenses, and working capital have been taken into account. The complex is designed to process 174,820 tons per stream day or 157,335 tons per calendar day (CD) of raw oil shale assaying 30 gallons of oil per ton of shale. Figure 1 is a block diagram of the total complex.

MINE DEVELOPMENT AND GENERAL MINING PLAN

Three mines will be operated to produce the required tonnage. At each mine, development will begin by driving three headings from the outcrop in the top bench of the minable section of the oil shale. These headings will be 30 feet wide by 31 feet high with 60-foot barriers between headings. One heading will be the main return airway, the center heading will be the belt haulage, and the right heading will be the intake airway and haulageway for men and supplies.

It is assumed that the development headings can be turned to the right at 600 feet and be clear of any weathering along the outcrop. The development headings will consist of three entries similar in size and functions to the main heading. The production panels will start operations as the development has advanced the required distance. It is estimated that 200 days will be required to open the first panel.

The mining plan is to mine the right side of the mine until the limits of mining are reached. The left side will be mined on the retreat. Under this system the mine will go into full production in the shortest possible time. It also means that the working area will be concentrated and better control of ventilation, haulage, and supervision will result.

Sufficient places will be provided to load tonnage. The crews will be equipped with a heading jumbo, scaling and bolting rig, bulldozer, front-end loader, and trucks.

The production panels are 1,860 feet by 1,020 feet and are mined using a 33-foot thick heading round and 28-foot bench round. The headings are 60 feet wide. Sixty-foot square pillars, regularly spaced, are left for support. A ramp will provide haulageway from the bench round to the main haulage level. Production panels will be equipped with a heading jumbo, a bench jumbo, scaling and bolting rigs, bulldozers, front-end loaders, and trucks.

The ore will be transported to portable crushers located at the mouth of the panel. These crushers will discharge onto a 60-inch belt that will carry the ore to the main haulage 60-inch belt.

The roof will be supported by roof bolts on 6-foot centers. Sixty-foot barriers will be left between panels and development on main headings.

Ventilation will be provided by 1 million cfm dual fans at the main portals. Direction of the airflow is controlled by crosscuts, regulators, and overcasts. Portable blowers with tubing provide secondary ventilation.

PRIMARY CRUSHING AND SCREENING PLANT

The run-of-mine shale is conveyed directly to the receiving hoppers at the crushing plant; one plant is provided for each of the three mines. The underground concrete hoppers are sized to provide 24-hour surge storage. The shale from the bottom of the hopper is conveyed to the primary-crusher feed bin at a rate of 58,272 tons per stream day or 2,428 tons per hour. A 90-percent onstream factor is assumed for the plants. Three conveyors, 48 inches wide and 200 feet long, are required. The shale is dumped into three parallel storage bins which are sized for 1/2-hour holdup. From the storage bins the shale is fed by magnetic vibratory feeders to the primary gyratory crushers where the size of the shale is reduced to minus 10.5 inches. The crushed shale is conveyed to underground surge bins (sized for 24-hour holdup).

The shale from the bottom of the surge bins is transported to the secondary crusher feed bins on 48-inch-wide belt conveyors.

SECONDARY AND TERTIARY CRUSHING AND SCREENING PLANTS

The shale at a rate of 58,272 tons per stream day is fed from the storage bins to three double hopper feed bins in the secondary crushing system. From each surge bin the shale is fed by two magnetic vibratory grizzly bar screens (six operating in parallel). The minus 4.5-inch material (47 percent of the total) falls through the screen to the product conveyor from the secondary crushers. The plus 4.5-inch material feeds to the secondary crushers (six crushers in parallel) and is crushed to minus 4.5 inches. The shale is then conveyed back under the screens, picking up the material that originally passed through the vibrating grizzlies, and is transported to tertiary crushing.

Three feed hoppers in tertiary crushing provide 20-minute holdup and receive the shale at a rate of 805 tons per hour for each hopper. Magnetic vibratory feeders (6 in parallel) are used to feed the vibrating screens (6 in parallel); the minus 3-inch material is screened out and falls on the product conveyors from the tertiary crushers. The plus 3-inch material (35 percent of the total) then feeds to the tertiary crushers (6 in parallel) where it is reduced in size to minus 3 inches. The shale is then transported by the return conveyors, picking up the material that passed through the 3-inch screens, to the main conveyor and is conveyed to three surge storage hoppers (3-day holdup).

From the surge storage hoppers 57,600 tons per stream day of shale is fed to the splitter in the screen house. Sixty-five percent of the shale bypasses the screens and feeds directly to the surge bin for feed to the retorting plant. The double-deck screens (three in parallel plus one spare) remove the minus 1-inch material on the top screen and minus 3/16-inch material on the bottom screen. The screens are fed by vibratory feeders. The shale from the top of the screens feeds to the conveyor that transports the bypass to the retorting plant and the fines from the screens (2,256 tons per stream day) are conveyed to the briquetting plant.

The overall dust losses in the crushing and screening operations are estimated to be 1.32 percent of the shale handled. Half of this loss is assumed to occur in crushing and transporting and the balance in screening.

BRIQUETTING PLANT

The fines are conveyed to the briquetting surge bin No. 1 on a 20-inch belt conveyor. The fine shale is then fed by vibratory feeders to two parallel hammer mills where it is reduced in size to minus 14 mesh. From the mills the shale is conveyed to surge bin No. 2. A vibratory pan feeder is used to feed the milled shale to two parallel double-paddle horizontal mixers where it is mixed with crude shale oil (binder). From the mixers the material flows by gravity into the briquetting machines.

The briquettes are then sent by conveyor to surge bin No. 3 and are then conveyed back to the retort feed conveyor.

RETORTING PLANT

The three retoring plants, each consisting of four 56-foot diameter units, will be located in close proximity to the three mine locations. The retorts are scaled up from smaller unit data but are assumed operable to facilitate this study.

The shale from the 3-hour surge bins and the briquettes from the briquetting plant are fed to the retort feed hoppers (atop the retorts). Each of the plants uses one belt conveyor equipped with an automatic tripper to feed the retorts.

The retorts are equipped with Cameron and Jones[1] improved feeding and discharge mechanisms. The feeding and discharge mechanisms are described in detail ("Quarterly of the Colorado School of Mines," v. 60, No. 3, July 1965) in a paper presented to the Second Oil Shale Symposium.[2]

Each retort processes 14,376 tons per stream day of shale and briquettes and produces 9,693.5 barrels per stream day of crude shale oil, 86,242,000 standard cubic feet per day of excess low-Btu gas, and 11,160 tons per stream day of spent shale.

The shale bed in the retorts is maintained at a depth of approximately 18 feet. The fresh feed at the top of the unit is preheated by the off gases from the retort combustion zone. The shale, at a rate of 500 pounds per hour per square foot of cross sectional area, moves through the preheat zone of the retort. The combustors, located near the midpoint of the shale bed, use recycled low-Btu gas burned with air to provide the heat needed for retorting.

About 82 percent of the recycled gas is fed to the bottom of the retort and is utilized to cool the spent shale to about 200° F prior to discharge. The remainder of the recycled gas, together with the combustion air, is fed directly to the combustors.

The gases from the top of the retorts, with entrained crude shale oil, flow through rotoclones and electrostatic precipitators for separation of gases and oil. The crude is then pumped to storage tanks located at the retorting site. The low-Btu gas is compressed either for recycle or to supply other plant fuel requirements.

The spent shale is fed to a common conveyor belt for discharge into a canyon. The mines and retort plants are located to provide dry canyons for the spent shale disposal. It is assumed that mined out areas will be utilized as soon as they become available. The crude shale oil from the retorts, 116,322 barrels per stream day, flows by pipeline to the refinery storage tanks near DeBeque, Colo.

PREREFINERY

The crude oil from storage is charged to a distillation column. The crude is heated in a furnace enroute to distillation. The crude charge is decomposed into a heavy fraction and vapors, about 50 percent bottoms and 50 percent overhead. The residual heavy fraction from the bottom of the distillation column is fed to the coke drums. The overhead product is cooled and depropanized to yield a distillate product, 55,100 barrels per stream day. The uncondensed gases, consisting of C_3 and lighter gases, are utilized for plant fuel. The liquid hydrogenated product, 42° API, is pumped to storage.

The bottoms from the distillation column are fed through a preheat furnace to the delayed coking units. The feed is preheated prior to being charged to the drums. The product from the top of the coker, the coker distillate, is cooled and depropanized and then, together with the distillation overheads, is charged to hydrogenation. The coke from the drums, 1,710 tons per calendar day, is stored for sale. The hydrocrackers operate at 835° F and 1,500 psig and produce a product containing about 45 volume percent material in the gasoline boiling range.

The gas streams from the hydrogenation, delayed coking, and distillation contain the sulfur and nitrogen available for recovery, the recoverable materials being in the form of hydrogen sulfide and ammonia. The streams are processed as follows: An ammonia-water wash is used to remove the hydrogen sulfide from the coker and distillation gases, and a water wash is used to extract the ammonia and hydrogen sulfide from the hydrogenation gas. The combined ammonia-hydrogen sulfide-water solution is then heated to 170° F to drive off the hydrogen sulfide which is scrubbed with sulfuric acid to remove traces of ammonia. The hydrogen sulfide is reacted with air in a Claus kiln to form sulfur (85.5 tons per calendar day) which is recovered as a hot liquid and stored for sale. The ammonia-water solution is pressurized to 230 psig and heated to 330° F to liberate the ammonia (275.5 tons per calendar day), which is cooled, condensed, and stored for sale in liquid form.

About 89 percent of the washed gas from the gas treating plant is steam reformed to produce the hydrogen needed for hydrocracking. The gas used for hydrogen generation is converted to produce 76 percent of the hydrogen theoretically available with complete conversion of the gas. A small amount of methane is purchased to augment the fuel supply. Using methane as an example (other hydrocarbons in the coker gas react in an analogous manner), the conversion involves the two following steps:

$$CH_4 + H_2O \rightarrow CO + 3H_2 \qquad (1)$$

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad (2)$$

with the following overall result:

$$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2 \qquad (3)$$

The first reaction takes place in tubes at 50 psig and 1,400° to 1,500° F using a nickel catalyst and an excess of steam. The endothermic heat of reaction is supplied by burning retort gas in the furnace surrounding the tubes. The hydrogen yield then is increased by catalytic water-gas shift conversion at 800° F as illustrated by equation 2. A hypersorber is used for hydrogen purification before compression and introduction to the hydrocracking unit. The hydrogen requirement is 1,662 standard cubic feet per barrel of product. Twenty-five percent excess hydrogen is produced to provide for surges and losses.

CAPITAL INVESTMENT

Table 1 is a summary of the estimated total capital investment required to develop the mines and to install the equipment to process 174,820 tons per stream day of oil shale. Included are initial catalyst and chemicals, interest during construction, startup expense, and working capital. The total estimated capital investment is $426,216,400.

WORKING CAPITAL

Working capital requirements are detailed in table 2. Interest during construction assumes a two-year construction period. An allowance of $11,033,100 is included for startup expenses.

The cost of providing steam, power, cooling water, sanitary water, compressed air, etc., is included in plant utilities. The cost of administrative buildings, roads, fences, rolling stock, etc., is included in plant facilities. A summary of utility and facility costs is given in table 3.

OPERATING COST

Table 4 is a summary of the estimated annual operating costs. Included in operating costs are labor, labor supervision, administration and general overhead, raw water charges, annual catalyst and chemicals, taxes, insurance, and depreciation. The annual operating cost is $85,543,000 before credit for the byproducts and $78,434,600 after credit.

FINANCIAL ANALYSIS

Table 5 shows the method of determining financial analysis based on a 12-percent discounted cash-flow rate which takes into account the present value of capital expenditures (both before and after startup). The present value of the positive cash flow includes the effect of changes after depreciation is taken. A selling price of $3.74 per barrel for the semirefined oil (30-gallon shale) is required to balance the present value of the capital expenditure with the present value of the positive cash flow, using a 12-percent compound and discount factors and a 20-year life.

Figure 2 illustrates the effect of varying the debt equity segment of the capital investment and the relationship of different values for the interest rate on the debt portion of the investment. This relationship is based on a selling price of $3.74 per barrel for the semirefined oil.

REFERENCES

1. Reference to specific makes or models of equipment is made to facilitate understanding and does not imply endorsement by the Bureau of Mines.

2. Russell J. Cameron. Cameron and Jones Vertical Kiln for Oil Shale Retorting. Pp. 131-146.

TABLE 1. - Capital investment summary, 30-gallon shale

Mine:	
Initial investment	$24,609,400
Present worth of deferred expense (discounted at 12 percent)	14,518,900
Retort plant:	
Retorting	115,381,100
Crushing and screening	12,316,000
Briquetting	1,582,000
Refinery	113,339,700
Utilities	41,469,400
Facilities	30,898,200
Total	354,114,700
Initial catalyst	9,517,700
Total plant cost	363,632,400
Interest during construction (plant)	16,225,200
Interest during development (mine)	561,700
Startup expense (plant)	11,033,100
Subtotal for depreciation	391,452,400
Working capital	34,764,000
Total	426,216,400

TABLE 2. - Working capital, 30-gallon shale

		Dollars
Cash	30 CD operating cost	6,952,800
Accounts receivable	90 CD operating cost	20,858,400
Inventory	30 CD operating cost	6,952,800
		34,764,000[1]

---

[1] Includes $5,944,100 for mine.

TABLE 3. - Summary, utilities and facilities, 30-gallon shale

	Utilities	Facilities
Retorting plant:		
Generator	$3,375,000	
Turbine	8,160,000	
Startup diesel generator set	1,080,000	
Power distribution	4,125,000	
Air compressor	3,582,000	
Gas compressor	1,582,200	
Steam generation and distribution	333,000	
Site preparation, etc		$1,500,000
Administration building		750,000
Subtotal	22,237,200	2,250,000
Refinery:		
Powerplant	9,100,000	
Power distribution	3,850,000	
Steam generation	5,200,000	
Air compression plant	750,000	
Telephone system	332,200	
Warehouse		480,100
Maintenance & operating building		266,700
Central shops		3,683,600
Intermediate gathering system		1,945,000
Water treatment and distribution (includes cooling water)		8,983,300
Condensate system		1,540,100
Laboratories		1,149,500
Operating unit buildings		2,937,600
Other refinery buildings		638,600
Refining site, roads, and fences		1,053,700
Sewage and refuse system		5,970,000
Subtotal	19,232,200	28,648,200
Total	41,469,400	30,898,200

TABLE 4. - Annual operating cost, 30-gallon shale

	Annual cost, dollars
Natural gas--3,610 Mscf/CD x 365 days/yr x $0.25/Mscf	329,400
Charge for use of water (Colorado)... ...480 M gph x 8,760 hr/yr x $0.026/M gal	109,300
Annual catalyst and chemicals	5,335,000
Direct labor plant	2,980,900
Direct labor supervision plant	540,000
Direct labor mine	5,282,500
Direct labor supervision mine	378,000
Maintenance labor plant	4,325,000
Maintenance labor supervision plant	420,000
Maintenance labor mine	1,526,300
Maintenance labor supervision mine	315,000
Operating supplies, mine	10,102,400
Operating supplies, plant (20% of plant maintenance)	1,814,000
Maintenance materials, plant (100% of maintenance labor)	4,325,000
Payroll overhead, mine (35% of payroll)	2,625,600
Payroll overhead, plant (25% of payroll)	2,066,500
Administration and general overhead, plant	1,235,900
Administration and general overhead, mine	1,293,800
Taxes (land valued at $1,000/acre, 6 sq miles) at 68 mills per dollar of evaluation	261,100
Taxes on improvement at mine (at 68 mills per dollar on 1/3 the cost)	557,800
Insurance, mine, 2% of investment	492,200
Taxes (retorting, crushing and screening, and interplant pipelines) at 68 mills per dollar on 1/3 the cost	3,485,300
Insurance (retorting, crushing and screening, and interplant pipelines) at 2% of investment	3,075,300
Taxes (refinery) at 68 mills per dollar on 1/3 the cost.	3,870,000
Insurance (refinery) at 2% of investment	3,414,800
Depreciation	25,381,900
Annual operating cost	85,543,000

Cost, dollars/barrel of oil = 85,543,000 $\div$ 36,500,000 = 2.34

$$\text{Cost, dollars/barrel of oil after byproduct credit} = \frac{85{,}543{,}000 - 7{,}108{,}400}{36{,}500{,}000}$$

$$= 2.15$$

TABLE 5. - Financial analysis, 30-gallon shale

Year	Estimated capital investment	Positive cash flow, oil at $3.74/bbl, dollars	Discount or compound factors, 12 percent	Present value investment, dollars	Present value cash flow, dollars	Federal income tax, dollars
-2	58,126,100	-	1.2544	72,913,400		
-1	269,549,100	-	1.120	301,895,000		
0	64,022,300	-	1.000	64,022,300		
1	-	61,011,100	.893		54,482,900	22,446,200
2	-	61,011,100	.797		48,625,800	22,446,200
3	-	61,011,100	.712		43,439,900	22,446,200
4	-	61,011,100	.636		38,803,100	22,446,200
5	5,481,200	61,011,100	.567	3,107,800	34,593,300	22,446,200
6	-	61,011,100	.507		30,932,600	22,446,200
7	-	61,011,100	.452		27,577,000	22,446,200
8	-	61,011,100	.404		24,648,500	22,446,200
9	-	61,011,100	.361		22,025,000	22,446,200
10	32,403,200	61,011,100	.322	10,433,800	19,645,600	22,446,200
11	-	61,011,100	.287		17,510,200	22,446,200
12	-	61,011,100	.257		15,679,900	22,446,200
13	-	61,011,100	.229		13,971,500	22,446,200
14	-	61,011,100	.205		12,507,300	22,446,200
15	6,369,600	61,011,100	.183	1,165,600	11,165,000	22,446,200
16		61,011,100	.163		9,944,800	22,446,200
17		50,018,500	.146		7,302,700	33,438,800
18	3,111,600	50,018,500	.130	404,500	6,502,400	33,438,800
19		50,018,500	.116		5,802,100	33,438,800
20	-34,764,000	50,018,500	.104	-3,615,500	5,201,900	33,438,800
Total				450,326,900	450,361,500	

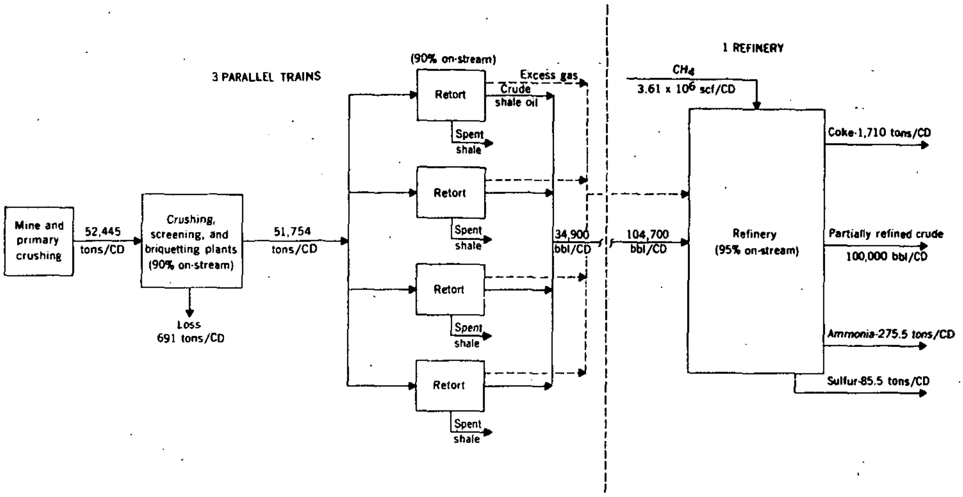
3 PARALLEL TRAINS
(90% on-stream)
Mine and primary crushing
52,445 tons/CD
Crushing, screening, and briquetting plants (90% on-stream)
Loss 691 tons/CD
51,754 tons/CD
Retort
Excess gas
Crude shale oil
Spent shale
34,900 bbl/CD
1 REFINERY
CH_4
3.61 x 10^6 scf/CD
104,700 bbl/CD
Refinery (95% on-stream)
Coke-1,710 tons/CD
Partially refined crude 100,000 bbl/CD
Ammonia-275.5 tons/CD
Sulfur-85.5 tons/CD

FIGURE 1. - General Block Diagram - Oil Shale Project, 100,000 Barrels per Calendar Day

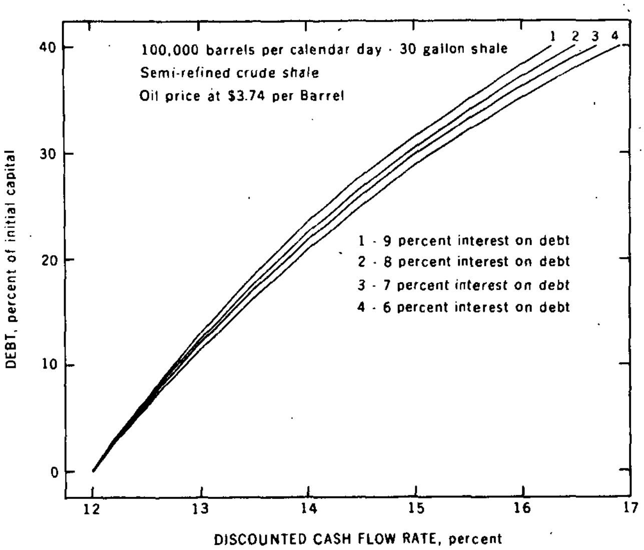

FIGURE 2. - The Effect of Debt-Equity Split on DCF at Various Interest Rates on Debt

REFINING OF CRUDE SHALE OIL PRODUCED BY IN SITU RETORTING

By

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INTRODUCTION

Crude shale oil produced in successful in situ combustion retorting experiments by the Bureau of Mines at Rock Springs, Wyo. (2,3) has characteristics that are somewhat different from those of shale oil crudes produced in either N-T-U or gas combustion retorts (1,9). Its gravity, pour point, and viscosity are such that it could be pipelined directly to a refinery without further processing. In addition to a lower specific gravity, viscosity, and pour point, this in situ crude oil contains more than twice as much naphtha and light distillate as gas combustion or N-T-U crudes. The in situ crude also shows a higher degree of saturation than the crudes produced by other processes. These properties indicate that in situ crude is similar to coker distillates from other crude shale oils.

In previous studies of the refinability of crude shale oils, either coking or prehydrogenation has been used as an initial step to reduce the viscosity and boiling range (5,10), or high-pressure hydrogenation with recycling of heavy ends has been used to produce catalytic reforming and catalytic cracking stocks (6-8). Because of the similarities between in situ crude shale oil and coker distillates obtained from other crude shale oils (4,10), the in situ crude should be amenable to refining methods used for coker distillates.

In 1956 the Bureau of Mines reported results of a refining study on coker distillate prepared by recycle, delayed coking of crude shale oil produced in an N-T-U retort (4). The present study describes similar experiments made with raw in situ shale oil produced at the Rock Springs, Wyo., in situ experiment (2,3). The refining involves hydrogenating that portion of the shale oil crude boiling above 400°F, hydrodenitrogenating and reforming the naphthas produced in the distillation and hydrogenation step, and catalytically cracking that portion of the hydrogenated heavy oil boiling above 400°F.

PROPERTIES OF IN SITU CRUDE SHALE OIL AND ITS DISTILLATE FRACTIONS

The crude shale oil used in this study was obtained from the in situ combustion retorting experiment at Rock Springs, Wyo., during the 3rd to 27th day of operation. A sample of the raw crude shale oil was dewatered and fractionated in a batch still equipped with a packed column, equivalent to 25 theoretical plates at total reflux. Properties of the crude shale oil and the various distillate fractions are shown in table 1.

The naphtha fraction from in situ crude shale oil is unstable, has a poor boiling range distribution, and contains undesirable quantities of sulfur and nitrogen. It has a low octane number despite the fact that it contains 26 volume percent aromatics. The diesel fuel is also unstable. It darkens rapidly on standing and has a high viscosity and carbon residue content. It contains less sulfur than the naphtha but considerably more nitrogen.

HYDROGENATION OF THE 400°F+ FRACTION

The total 400°F+ fraction from the in situ crude oil was hydrogenated over a presulfided cobalt molybdate catalyst in a fixed-bed, bench-scale unit, the flow diagram of which is shown in figure 1. The oil was mixed with 2,700 scf of hydrogen per barrel and passed downflow over the catalyst bed contained in a stainless steel reactor heated by a four-zone electric furnace. Pressure was maintained at 1,100 psig by means of a back pressure regulator, and liquid product was collected in a separator maintained at 200 psig. Tail gas from the separator was metered and sampled. The hydrogenation was accomplished in a continuous 96-hour run. No deactivation of the catalyst was evident from analyses of the products taken at various time intervals during the run. Processing conditions and product yields are shown in table 2.

Calculations based on the amounts of hydrogen charged to the unit and recovered in the products indicate that 1,145 scf of hydrogen per barrel was used in the hydrogenation step. This quantity is of the same order as that reported by Carpenter and coworkers (4) for hydrogenation of the 400°F+ fraction from N-T-U coker distillate. The amount of hydrocracking occurring during the hydrogenation was not excessive since only about 20 volume percent of the feed was converted to products boiling below 400°F as compared to the 45 volume percent reported for hydrogenation of the 400°F+ fraction of N-T-U coker distillate. About 75 percent of the nitrogen and 90 percent of the sulfur were removed from the charge stock by hydrogenation. These values are only slightly lower than those obtained by Carpenter and coworkers on the coker distillate from N-T-U crude at a slightly higher operating temperature.

The total liquid product from the hydrogenation step was separated into light naphtha, heavy naphtha, and 400°F+ bottoms in the same equipment used to fractionate the original in situ crude. Properties of the charge stock and liquid fractions are shown in table 3.

The heavy naphtha fraction had a research octane number of 55.4 and contained 0.28 weight percent nitrogen and 0.01 weight percent sulfur. The 400°F+ fraction contained 0.56 weight percent nitrogen and 0.02 weight percent sulfur.

HYDRODENITROGENATION (HDN) OF NAPHTHA

The heavy naphtha from the hydrogenation of the 400°F oil was combined with the raw naphtha from the distillation of the original crude. The combined naphtha was then hydrodenitrogenated over a presulfided nickel-tungsten catalyst in the same unit used for the hydrogenation step. Processing conditions used and product yields are shown in table 4. Properties of naphtha charge stock and the HDN product are shown in table 5.

The yield of naphtha from the HDN step was 103.96 volume percent. Considerable saturation occurred during the HDN step since olefins were completely eliminated and the aromatic content was reduced from 23 to 5.5 volume percent. This is also apparent from the lower octane number of 36.4. Nitrogen was reduced from 0.9 weight percent to 4 ppm. This reduction may partially account for the increase in the amounts of lower boiling components in the naphtha after HDN.

REFORMING OF NAPHTHA

The total liquid product from the HDN step was used as feedstock for reforming. A 20-ml bed of fresh Engelhard RD-150 reforming catalyst contained in a 9/16-inch I.D. stainless steel reactor was used. Reforming was carried out at 859°F, 500 psig, a liquid hourly space velocity of 3.0, and a hydrogen feed rate of 3,500 scf of hydrogen per barrel. Liquid products were collected in a separator maintained at 200 psig, and were stabilized to yield reformate and gases composed of butanes and lighter components. Octane numbers were obtained on the stabilized reformate. Operating conditions and product yields are shown in table 6, and properties of the reformate are given in table 7.

The liquid and hydrogen yields, octane numbers, and yield octane numbers are consistent with those found by other investigators when reforming shale oil naphthas under similar conditions (10). It is reasonable to expect that higher reforming temperatures would result in reformates with higher octane numbers.

CATALYTIC CRACKING OF 400°F+ HYDROGENATE

The 400°F+ bottoms from the hydrogenation of the 400°F+ crude oil were catalytically cracked in a fixed-bed laboratory unit. The oil was preheated in a tube furnace and passed downflow over a bed of Houdry HZ-1 catalyst contained in a stainless steel reactor heated by a four-zone electric furnace. Reactor effluent was cooled by exchange with tap water and was collected in a separator maintained at 32°F. Tail gas passed through a cold trap cooled with Dry Ice and into a gas holder. Gas and light ends were analyzed by GLC. Coke deposits were determined by analysis of the regeneration gases.

Cracking was carried out at 900°F, atmospheric pressure, and a liquid hourly space velocity of 0.8. Oil was charged to the unit until a catalyst to oil ratio of 4 was reached. Operating conditions used and product yields obtained are shown in table 8, and properties of the liquid products are shown in table 9. A total yield of 40.95 volume percent gasoline was calculated as the sum of observed gasoline volumes plus additional volumes potentially available from alkylation of propylenes and butenes.

At the 50-percent conversion level the gasoline had a high octane number of 99 + RON + 3 and represented 21.08 volume percent of the raw shale oil.

SUMMARY AND CONCLUSIONS

Refining tests made on crude shale oil produced in the Rock Springs, Wyo., in situ experiment showed that its refinability is similar to those of coker distillates made from other crude shale oils. A summary of product yields for the set of operating conditions used is shown in table 10. No attempt was made to optimize the refining conditions used since the object of these experiments was to compare the refining characteristics of total in situ crude shale oil with those of a coker distillate refined under similar conditions. The use of higher temperatures and pressures during the hydrogenation of the 400°F+ fraction would undoubtedly reduce the nitrogen content of the catalytic cracking stock and increase the amount of gasoline available for reforming.

ACKNOWLEDGMENTS

The work upon which this report is based was done under a cooperative agreement between the Bureau of Mines, U.S. Department of the Interior, and the University of Wyoming. Mention of specific brand names is made for information purposes only and does not imply endorsement by the Bureau of Mines.

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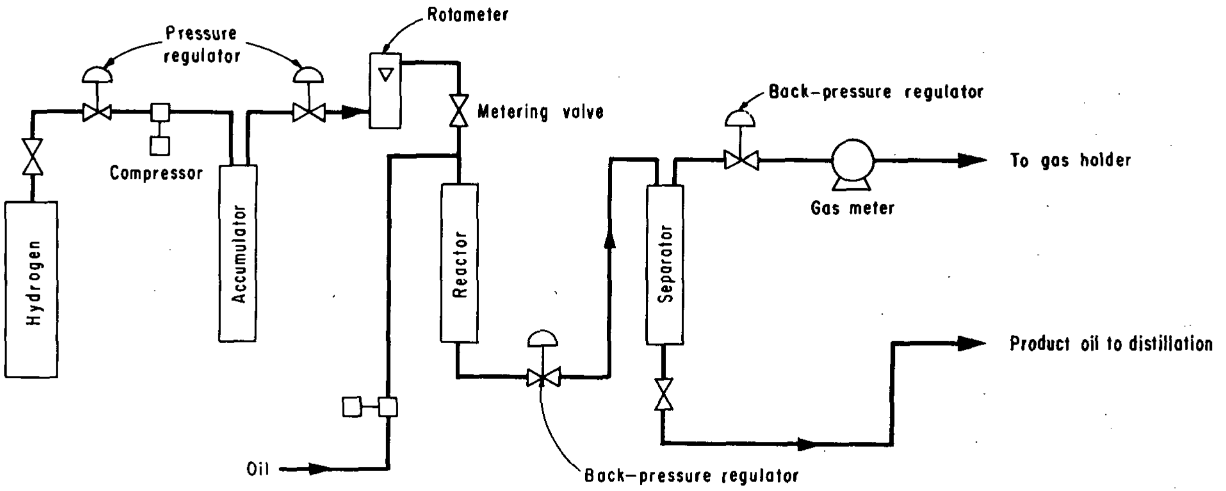
Pressure regulator
Rotameter
Metering valve
Back-pressure regulator
Compressor
Hydrogen
Accumulator
Reactor
Separator
Gas meter
To gas holder
Product oil to distillation
Oil
Back-pressure regulator

FIGURE I.– Simplified Flow Diagram of Hydrogenation Unit.

OSCR-69-40

TABLE 1. - Properties of Rock Springs, Wyo., in situ crude shale oil and its distillate fractions

	Crude	Naphtha	Diesel	650°F+
Yield, vol pct	100	25.57	45.73	28.70
Gravity, °API	28.4	44.1	30.5	15.6
Carbon, wt pct	84.88	84.32	85.38	84.58
Hydrogen, wt pct	12.02	13.66	12.04	10.87
Nitrogen, wt pct	1.69	1.23	1.55	2.17
Sulfur, wt pct	0.60	0.66	0.59	0.50
Oxygen, wt pct	0.80	0.13	0.44	1.83
Pour point, °F	10	-	<5	-
Viscosity, SUS at 100°F	45	-	38	-
Carbon residue, wt pct	1.7	-	[1]1.2	2.4
Ash, wt pct	0.01	-	[1]0.03	0.05
ASTM distillation, °F at 760 mm:				
IBP	241	239	428	-
5 pct recovered	348	290	451	-
10	383	303	460	-
20	422	314	474	-
30	460	326	485	-
40	498	336	494	-
50	537	346	508	-
60	575	356	522	-
70	625	365	542	-
80	665	375	563	-
90	-	387	595	-
95	-	398	614	-
EP	673	408	631	-
Recovery, vol pct	83.0	98.5	98.5	-
Octane numbers:				
Research, clear	-	57.9	-	-
+ 3 ml TEL	-	59.4	-	-
Hydrocarbons, vol pct:				
Paraffins + naphthenes	-	56	-	-
Olefins	-	18	-	-
Aromatics	-	26	-	-

[1] 10 percent bottoms.

TABLE 2. - Hydrogenation of 400°F+ in situ shale oil

Operating conditions:	
Temperature, °F	815
Pressure, psig	1100
Space velocity, V_o/V_c/hr	0.72
Catalyst	Co-Mo
Hydrogen feed, scf/bbl	2700
Hydrogen consumed, scf/bbl	1145

Product yields:	Percent of feed		Percent of crude	
	wt	vol	wt	vol
Liquid product	95.60	102.40	73.28	76.22
C_5 - 160°F	1.14	1.69	0.87	1.26
160° - 400°F	16.33	18.79	12.52	13.99
400°F+	78.13	81.92	59.89	60.97
Coke	0.13		0.10	
Hydrogen	-1.92		-1.47	
Methane	0.80		0.61	
Ethane	0.84		0.64	
Propane	0.78		0.60	
Isobutane	0.12	0.19	0.09	0.14
Butane	0.41	0.63	0.31	0.47
Butenes	0.09	0.13	0.07	0.10
Ammonia	1.63		1.25	
Hydrogen sulfide	0.59		0.45	
Water	0.92		0.71	

TABLE 3. - Properties of charge stock and products from hydrogenation of 400°F+ oil from in situ crude

	Charge	Total liquid product	Light naphtha C_5-160°F	Heavy naphtha 160°-400°F	400°F+
Properties:					
Gravity, °API	25.1	36.6	80.0	48.5	32.5
Carbon, wt pct	85.19	86.24	83.42	86.16	86.32
Hydrogen, wt pct	11.61	13.22	16.49	13.53	13.11
Nitrogen, wt pct	1.87	0.48	0.03	0.28	0.56
Sulfur, wt pct	0.59	0.06	0.06	0.01	0.02
Hydrocarbons, vol pct:					
Paraffins	-	-	94.1	53.6	-
Naphthenes	-	-	2.4	29.8	-
Olefins	-	-	0.0	0.0	-
Aromatics	-	-	3.5	16.6	-
ASTM distillations, °F at 760 mm:					
IBP	-	168	-	199	434
5 pct recovered	437	332	-	244	461
10	457	387	-	261	467
20	483	437	-	275	478
30	510	465	-	298	495
40	534	486	-	306	512
50	573	508	-	316	538
60	614	532	-	326	567
70	657	561	-	340	602
80	678	598	-	352	638
90	-	644	-	365	-
95	-	694	-	375	-
EP	679	694	-	381	661
Recovery, vol pct	83.5	95.0	-	98.0	87.0
Octane numbers:					
Research, clear	-	-	-	55.4	-
+ 3 ml TEL	-	-	-	75.2	-

TABLE 4. - Hydrodenitrogenation of naphtha

Operating conditions:				
Temperature, °F	700			
Pressure, psig	1500			
Space velocity, V_o/V_c/hr	1.07			
Catalyst	Ni-W			
Hydrogen feed, scf/bbl	5000			
Hydrogen consumed, scf/bbl	649			
Product yields:	Percent of feed		Percent of crude	
	wt	vol	wt	vol
Liquid product	98.72	103.96	35.41	41.13
Coke	0.03		0.01	
Hydrogen	-1.23		-0.44	
Methane	0.03		0.01	
Ethane	0.22		0.08	
Propane	0.42		0.15	
Isobutane	0.11	0.16	0.04	0.06
Butane	0.14	0.20	0.05	0.08
Ammonia	1.09		0.39	
Hydrogen sulfide	0.47		0.17	

TABLE 5. - Properties of HDN charge and product naphthas

	Charge	Product
Properties:		
Gravity, °API	44.8	54.2
Carbon, wt pct	84.96	84.98
Hydrogen, wt pct	13.61	15.02
Nitrogen, ppm	9000	4
Sulfur, wt pct	0.43	0.00
Hydrocarbons, vol pct:		
Paraffins	65	56.1
Naphthenes		38.4
Olefins	12	0.0
Aromatics	23	5.5
ASTM distillation, °F at 760 mm:		
IBP	203	175
5 pct recovered	257	237
10	273	252
20	294	268
30	309	281
40	323	301
50	336	317
60	346	331
70	357	343
80	367	358
90	379	377
95	389	395
EP	400	404
Recovery, vol pct	98.0	97.3
Octane numbers:		
Research, clear	57.0	36.4
+ 3 ml TEL	-	59.3

TABLE 6. - Reforming of HDN naphtha

Operating conditions:	
Temperature, °F	859
Pressure, psig	500
Space velocity, V_o/V_c/hr	3.01
Catalyst	RD-150
Hydrogen feed, scf/bbl	3500
Hydrogen yield, scf/bbl	951

Product yields:	Percent of feed		Percent of crude	
	wt	vol	wt	vol
Liquid product	91.85	89.61	32.52	36.86
Hydrogen	1.89		0.67	
Methane	0.48		0.17	
Ethane	1.44		0.51	
Propane	2.54		0.90	
Propylene	0.05	0.06	0.03	0.03
Isobutane	0.65	0.88	0.23	0.36
Butane	1.10	1.46	0.39	0.60

TABLE 7. - Properties of reformate

ASTM distillation, °F at 760 mm:	
IBP	141
5 pct recovered	201
10	230
20	259
30	275
40	290
50	308
60	318
70	330
80	340
90	357
95	375
EP	383
Recovery, vol pct	96.5
Octane numebers:	
Research, clear	73.0
+ 3 ml TEL	90.0

TABLE 8. - Catalytic cracking of 400°F+ hydrogenate

	Percent of feed		Percent of crude	
Operating conditions:				
Temperature, °F	899			
Pressure	Atmospheric			
Space velocity, V_o/V_c/hr	0.8			
Catalyst	HZ-1			
Product yields:	wt	vol	wt	vol
Liquid product	76.34	81.01	45.72	55.81
C_5 - 400°F	24.54	30.60	14.70	18.66
400°F+	51.80	50.41	31.02	30.74
Coke	7.21		4.32	
Hydrogen	0.47		0.28	
Methane	1.27		0.76	
Ethane	1.29		0.77	
Ethylene	0.65		0.39	
Propane	2.74		1.64	
Propylene	2.24	3.73	1.34	2.27
Isobutane	4.46	6.88	2.67	4.20
Butane	1.50	2.24	0.90	1.36
Butenes	1.84	2.42	1.10	1.48

TABLE 9. - Properties of products from catalytic cracking of 400°F+ hydrogenate

	C_5-400°F	400°F+
ASTM distillation, °F at 760 mm:		
IBP	107	410
5 pct recovered	123	435
10	140	439
20	155	448
30	180	455
40	228	467
50	256	479
60	281	506
70	296	526
80	318	-
90	344	-
95	365	-
EP	373	530
Recovery, vol pct	96.0	71.5
Octane numbers:		
Research, clear	90.9	-
+ 3 ml TEL	99.2	-

TABLE 10. - Summary of yields from refining of in situ crude shale oil

Process[1], wt pct	A	B	C	D	Totals
C_5 - 160°F gasoline	0.87				0.87
Reformate			32.52		32.52
CC gasoline				14.70	14.70
400°F+ recycle oil				31.02	31.02
Coke	0.10	0.01		4.32	4.43
Hydrogen	-1.46	-0.44	0.67	0.28	-0.95
Methane	0.61	0.01	0.17	0.76	1.55
Ethane	0.64	0.08	0.51	0.77	2.00
Ethylene				0.39	0.39
Propane	0.60	0.15	0.90	1.64	3.29
Propylene			0.03	1.34	1.36
Isobutane	0.09	0.04	0.23	2.67	3.03
Butane	0.31	0.05	0.39	0.90	1.65
Butenes	0.07			1.10	1.17
Ammonia	1.25	0.39			1.64
Hydrogen sulfide	0.45	0.17			0.62
Water	0.71				0.71
					100.95

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[1] A. Hydrogenation of 400°F+ in situ crude at 815°F, 1100 psig, and 0.72 LHSV.

B. Hydrodenitrogenation of raw naphtha and 160°-400°F naphtha from A at 700°F, 1500 psig, and 1.1 LHSV.

C. Reforming of naphtha from B at 500 psig, 859°F, and 3 LHSV to yield 89.6 vol pct of 90 RON + 3 reformate.

D. Catalytic cracking of 400°F+ oil from A at 899°F and 0.8 LHSV.

THE EFFECT OF MILD OXIDATION ON THE QUALITY OF A SHALE-OIL NAPHTHA FRACTION

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INTRODUCTION

Green River shale-oil naphthas have several properties that make them require extensive refining before they can be utilized. These properties include high levels of sulfur, nitrogen, and olefinic compounds. Although Green River shale-oil naphtha is similar in hydrocarbon composition to thermally cracked petroleum naphthas, a higher nitrogen content of the shale-oil naphtha [typically about 1 weight-percent (1)[1]] distinguishes it from cracked petroleum naphthas. Another distinguishing characteristic of shale-oil naphtha is its higher reactivity to oxygen compared to thermally cracked petroleum naphthas. In one case, this high reactivity to oxygen was reported to cause the formation of as much as 10 weight-percent of high-molecular-weight gum containing 7 to 8 weight-percent nitrogen (2). This facile reaction with oxygen, which concentrates nitrogen in easily removable heavy products, suggests that oxidation of shale-oil naphthas might be employed to improve the quality of the naphtha.

To explore this possibility, a fraction boiling at 140° to 150° C and selected for its high nitrogen content and instability was distilled from a heavy shale-oil naphtha and portions of this fraction, hereafter called the naphtha fraction, were allowed to react with measured amounts of oxygen under mild conditions. Samples taken during the reactions were separated into gum and volatile material by vacuum distillation and the volatile material, hereafter called oxidized naphtha, was analyzed. The effect of oxidation on nitrogen content and major hydrocarbon groups was assessed. Also the susceptibility of an oxidized naphtha to further oxidation was investigated, and an oxidation experiment was conducted on the naphtha fraction after its nitrogen content was reduced by silica-gel treatment. This paper describes the results of these experiments.

EXPERIMENTAL PROCEDURE

Preparation of Naphtha Fraction

The source of the naphtha fraction was a heavy naphtha from Green River shale oil produced in an internally fired retort. Based on preliminary testing and analyses of narrow boiling fractions of the heavy naphtha, material boiling at 140° to 150° C (760 Torr) was selected for study. This material, which had a high nitrogen content and showed high reactivity toward oxygen, was distilled from the source naphtha in a simple glass distillation apparatus under nitrogen protection. About 1.5 liters of this fraction were redistilled in a jointless all-Pyrex glass bulb-to-bulb vacuum distillation apparatus at 10^{-6} Torr. The water-white, gum-free distillate was divided into samples of convenient size by pouring into glass ampoules under vacuum. The flame-sealed ampoules were stored in the dark until used for analyses or oxidation experiments. This naphtha fraction had a nitrogen content of 1.26 weight-percent.

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[1] Underlined numbers in parentheses refer to items in the list of references at the end of this report.

Oxidation Apparatus

The apparatus consisted of an oxidation vessel, electrolytic oxygen supply system, and associated valves and tubing. The oxidation vessel was a flat-bottomed, wide mouthed, cylindrical glass vessel equipped with a water jacket and fitted with a glass head with access ports for introduction of sample and gas. The head was sealed to the main body by an O-ring.

The electrolytic oxygen supply system consisted of an electrolysis cell, constant current DC supply, AC control circuit, drying tower, and check valve. The electrolysis cell, made of Pyrex glass and equipped with platinum electrodes, was essentially two concentric cylindrical chambers held vertical by a clamp. The outer chamber, containing the negative electrode, was a cylinder, 55 mm ID and 120 mm high, open at the top. Hydrogen released in this chamber was vented to the atmosphere. The inner chamber, 30 mm ID by 110 mm high, closed at the top and ring-sealed to the outer chamber at the bottom, vented to the oxidation system through an inner concentric tube, 10 mm in diameter, ring-sealed at the bottom of the chamber, and extending to near the top of the inner chamber. A hole in the wall of the inner chamber near the bottom allowed free flow of the 0.5 N sulfuric acid electrolyte between the inner and outer chambers of the cell. Electrolyte level was maintained below the top of this inner concentric tube. Oxygen released at the positive electrode in the inner chamber rose to the surface of the electrolyte and passed out of the cell through the inner concentric tube. This tube extended from the bottom of the cell and ended in an O-ring joint by which the cell was attached to the system.

The electrolysis cell was powered by a Sorensen QRB 20-1.5 DC supply,[2] wired for constant current operation that was turned on and off by an AC control circuit. This circuit included a relay, a General Electric elapsed-time meter displaying minutes and tenths, and a platinum wire contact that functioned as a pressure switch. This contact was set to touch the electrolyte surface in the cell outer chamber at equilibrium pressure, completing a circuit that held the relay contacts open. A drop in system pressure, causing the electrolyte level to rise in the inner cell chamber and drop in the outer cell chamber, broke the contact, allowing the relay points to close the AC circuit to the timer and power supply. Oxygen generated in the cell inner chamber restored system pressure to equilibrium and remade the contact, thus shutting off the power supply and timer. This cell and control arrangement were adapted from a system used for measuring biological oxygen demand (3).

Oxygen from the cell was dried by passing through 2 A molecular sieves in a water-jacketed glass tower, 25 mm ID by 150 mm high. The drying tower outlet was connected to a water-jacketed glass check valve that prevented back flow through the oxygen supply system. This valve was a low-form, flat-bottomed, closed chamber with a vertical capillary inlet dipping 1 mm into a pool of mercury, and an outlet side arm above the mercury level that connected to the manifold.

The system components were connected in series by 1/8 inch OD Teflon tubing and stainless steel pressure fittings to form a gas-tight manifold. Stainless steel valves in the system permitted isolation of major components, control of gas flow, and provided access for pressure adjustment and gas inlet.

Auxiliary equipment included two Brinkmann/Lauda K2R circulating water baths, a Cole-Parmer 9" x 9" magnetic stirrer, and a Teflon-covered stirring disk. One bath controlled the temperature of the oxidation vessel; the other bath controlled the temperature of the drying tower and check valve. The magnetic stirrer activated a stirring disk that agitated the naphtha sample during oxidation experiments.

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[2] Reference to specific brand names is made for identification purposes only and does not imply endorsement by the Bureau of Mines to the exclusion of others that may be suitable.

Oxidation Experiment

In a typical experiment, the circulating baths were adjusted to the desired temperatures (20° or 25° C), and the apparatus was evacuated and refilled with dry oxygen three times. During this operation, the cell contained no electrolyte and was plugged with a rubber stopper. The apparatus was evacuated through a port on the reaction vessel, and cylinder oxygen was admitted through the drying tower. With the system filled with oxygen at slightly above atmospheric pressure, the cell was unstoppered and filled with electrolyte. After adjusting the liquid in the inner and outer chambers to the same level, the platinum wire contact of the control circuit was adjusted to touch the electrolyte surface. The oxidation vessel was then shut off from the manifold and flushed with air. A weighed sample of the naphtha fraction was poured into the vessel through the sample introduction port and stirred 5 minutes with the port open. During this period the electrical system was turned on, pressure was reduced slightly in the oxygen supply system, the cell current was adjusted to 700 mA, and the system was brought to atmospheric pressure by cell operation. When the cell shut off, the sample port was closed, the elapsed time meter was set to zero, the vessel was opened to the manifold, and the time was recorded. At intervals throughout the run, the time and the reading of the elapsed-time meter were recorded. The quantity of oxygen supplied was calculated from the value of the cell current and the reading of the elapsed time meter, using Faraday's law.

The reaction mixture was sampled by syringe and needle several times in the first 24 hours of reaction and thereafter at random intervals of 24 to 72 hours. Each sample was transferred to an ampoule that was then attached by means of a stainless steel O-ring fitting to a vacuum transfer manifold. The sample was freeze-thaw degassed, the oxidized naphtha was distilled at room temperature and 10^{-6} Torr into another ampoule immersed in liquid nitrogen, and the ampoules were sealed off by flame.

At the end of the run the oxidation vessel was shut off from the manifold and the reaction mixture was allowed to stand 1 hour without agitation. The liquid was then decanted into an ampoule and was distilled in the same manner as earlier samples.

Analytical Methods

Total nitrogen was determined by microcoulometry (4) or the Kjeldahl method (5). Basic nitrogen was determined by potentiometric titration with 0.1 N perchloric acid-dioxane solution using a solvent medium composed of equal volumes of benzene and acetic anhydride (6).

A silica-gel adsorption method (7) was employed to determine hydrocarbon groups. Samples were not treated to remove tar acids and bases before analysis (a modification of the published method).

RESULTS AND DISCUSSION

The results of the study demonstrate that the shale-oil naphtha fraction is much more reactive toward oxygen than is an unstable petroleum distillate. Furthermore, quantitative assessment of chemical changes in the naphtha fraction indicates that oxidation may be exploited as a means of improving shale-oil naphtha. A silica-gel adsorption treatment provided evidence of the constituents that are responsible for the instability of the naphtha fraction.

Selected properties of the naphtha fraction of this study, the heavy shale-oil naphtha from which it was separated, an NTU shale-oil naphtha, and an unstable thermally cracked petroleum naphtha are shown in table 1. The table gives the sulfur and nitrogen contents and the hydrocarbon composition of the materials. The thermally-cracked petroleum distillate chosen for this comparison,

TABLE 1. - Selected properties of three shale-oil distillates and an unstable petroleum distillate

Distillate type	Boiling range, °C	Sulfur, wt pct	Total nitrogen, wt pct	Basic nitrogen, wt pct	Hydrocarbon composition, vol pct		
					Saturates	Olefins	Aromatics
S.O. naphtha fraction (this work)	140-150	0.66	1.26	1.08	28	42	30
S.O. heavy naphtha	139-227	.87	1.53	1.20	28	49	23
NTU S.O. naphtha	67-213	1.24	1.21	1.00	30	48	22
TC[1] California dist. No. 126	189-368	1.19	.37	.18	34	21	45

[1] Thermally cracked.

although not typical of all thermally cracked petroleum naphthas, had properties similar to those of the shale-oil naphthas. This distillate had the highest nitrogen content and oxygen susceptibility of the 34 distillate fuels that were investigated in another stability study (8). The properties shown for the shale-oil naphthas, and in particular the high nitrogen and olefin contents, are typical for Green River shale-oil naphthas. Although most of the nitrogen is in the basic form (6), the difference between total nitrogen content and basic nitrogen content is probably pyrrole nitrogen. In the case of the naphtha fraction of this study, some confirming evidence for the presence of pyrroles was shown by the presence of an N-H stretching vibration in the infrared spectrum.

The first part of the research was a quantitative comparison of the rates of oxygen consumption by the naphtha fraction to the rate of oxygen consumption of the petroleum distillate of table 1. Oxygen absorption curves for the petroleum distillate at 66° C (8) and for the naphtha fraction at 20° and 25° C are shown in figure 1. The curves for the naphtha fraction, representing three oxidation runs at 20° C and two runs at 25° C, are the best that could be drawn through all data points. It can be seen that in 40 hours the naphtha fraction at 20° C had absorbed as much oxygen as the petroleum distillate at 66° C. At 25° C, the naphtha fraction absorbed more than twice as much oxygen in 40 hours as the petroleum distillate. The difference is especially notable when one considers that the petroleum distillate selected for this comparison represents an extreme case found among petroleum distillates for which oxygen consumption data are reported.

The effect of oxygen absorption on both the total nitrogen content and the basic nitrogen content was examined. Figure 2 shows the quantitative effect on these concentrations as oxygen is absorbed. In this figure, oxygen and nitrogen are expressed in moles per liter of naphtha. Early in the reaction, absorption of 0.04 mole of oxygen per liter of naphtha results in a total decrease of 0.07 mole of nitrogen per liter, but basic nitrogen is reduced only 0.04 mole per liter; the difference represents a reduction of 0.03 mole of nonbasic nitrogen per liter. Because nonbasic nitrogen is attributed to pyrroles, these data give indirect evidence of the early participation of pyrroles in the oxidation process. As the reaction progresses, basic nitrogen concentration decreases linearly in the ratio 0.4 mole of basic nitrogen per mole of oxygen absorbed. Total nitrogen concentration decreases somewhat more slowly, approaching half of the original concentration of total nitrogen. The resulting divergence of the two curves near the end of the reaction period reflects a buildup of nonbasic nitrogen compounds during the oxidation and a gradual decrease in the efficiency of nitrogen removal. The results of these experiments show that the concentration of total nitrogen was reduced 45 percent and the concentration of basic nitrogen was reduced 48 percent upon absorption by the naphtha of 0.3 mole of oxygen per liter. The gum recovered at this oxidation level amounted to about 8 weight-percent of the starting material. Thus nitrogen was concentrated in heavy products easily removed from the mixture by distillation. These data indicate the possible utility of the mild oxidation reaction for improving the quality of shale-oil naphthas through nitrogen removal.

Hydrocarbon analyses were made on the original naphtha fraction and on oxidized naphtha at two levels of oxidation. The results of these analyses are given in table 2. The analyses show that the oxidation results in a loss of both olefinic and aromatic compounds relative to saturates, which are assumed not to react. The aromatic portion of the naphtha decreased faster initially than did the olefinic portion. This effect is partly due to the formation of heavy products from reactive substances such as pyridines, pyrroles, and sulfur compounds during the oxidation. These compounds are measured in the aromatic portion of the naphtha in the method of analysis used [silica-gel displacement (7)]. As the oxidation progresses, the olefin concentration declines more rapidly than the aromatic concentration, shown by the relatively sharp decrease in the olefin-saturate ratio. The nitrogen content at the highest level shown was 0.75 weight-percent, or about 60 percent of the original concentration.

TABLE 2. - Hydrocarbon analysis of a 140° to 150° C shale-oil naphtha fraction at different levels of oxidation

Oxygen absorbed, moles/liter x 10^3	Hydrocarbon analysis, vol pct			Olefins / saturates ratio	Aromatics / saturates ratio
	Saturates	Olefins	Aromatics		
0	30	40	30	1.33	1.00
171	33	43	24	1.30	.73
247	39	37	24	.95	.62

A test of the stability of the oxidized shale-oil naphtha was made by subjecting an oxidized naphtha to a second oxidation. The oxidized naphtha, containing 0.82 weight-percent nitrogen, was reoxidized at 20° C. It exhibited a rate of oxidation about one-fourth that of the original fraction. Oxygen absorbed in the first 60 hours was about 11×10^{-3} moles per liter compared with 42×10^{-3} moles per liter by the original material in the same period. This test shows the improvement in quality over the original naphtha as measured by stability to further oxidation brought about by the first oxidation. This apparent stabilization of the naphtha by oxidation may be due to the removal of reactive components or to the formation of substances that inhibit oxidation, or both. The selective removal of nitrogen compounds in the form of heavy oxidation products suggests that nitrogen compounds are important reactive components. Consequently, removal of nitrogen compounds from the naphtha fraction should lower its reactivity toward oxygen.

To examine this possibility, part of the nitrogen was removed from the naphtha fraction by silica-gel adsorption. The method was essentially the same as that used for hydrocarbon group analysis (7), scaled up to accommodate a large (134-gram) sample. The first 91 percent of the naphtha fraction (122 grams) that emerged from the column was collected. This method reduced the nitrogen content from 1.26 to 0.67 percent. When this material was subjected to mild oxidation, the oxygen absorption curve was found to be nearly the same as that for the reoxidized shale-oil naphtha. A comparison of the two absorption curves is shown in figure 3. The slightly higher rate of the silica-gel-treated sample is probably due to the slightly higher temperature of this oxidation (25° C compared with 20° C for the oxidized shale-oil naphtha). This experiment showed that mild oxidation of the naphtha was as effective as the use of adsorbents for improving the quality of the naphtha. The use of oxygen (air) in a commercial process would probably be more economical than the use of adsorbents. This experiment also indicates that nitrogen compounds are important reactive components, and demonstrates the beneficial effects of lowering the nitrogen concentration of the naphtha.

The possibility that oxidized naphtha contains oxidation products that inhibit further oxidation is being investigated. Efforts are being made to isolate and identify the volatile nonbasic-nitrogen-containing products whose formation is indicated by the divergence of the curves in figure 2. The role of individual nitrogen compounds in the oxidation process and the composition of the heavy oxidation products are also under investigation.

CONCLUSION

The results of this preliminary study indicate that mild oxidation of shale-oil naphthas could be used to improve the quality of the naphthas. The mild oxidation results in a significant reduction in the quantity of undesirable nitrogen compounds, leading to a naphtha of improved stability towards further oxidation. The oxidation treatment may provide a better quality naphtha for further processing into usable fuels.

ACKNOWLEDGMENT

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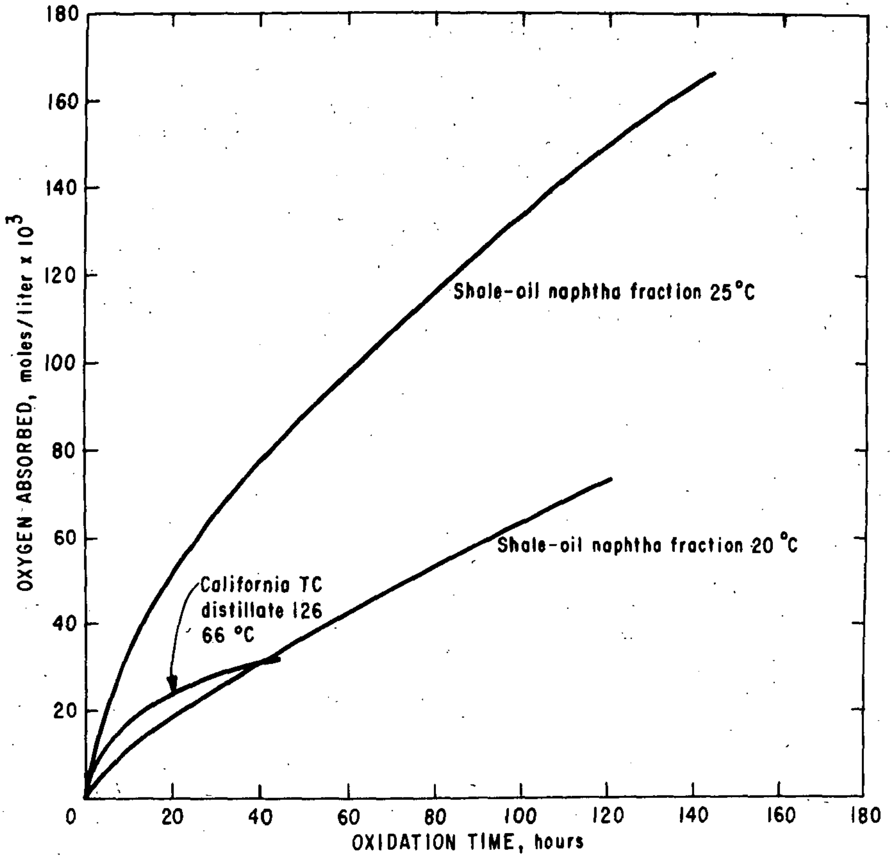

FIGURE 1.-Oxygen Absorption Curves for a Shale-Oil Naphtha Fraction And an Unstable Petroleum Distillate.

SOA-528 P

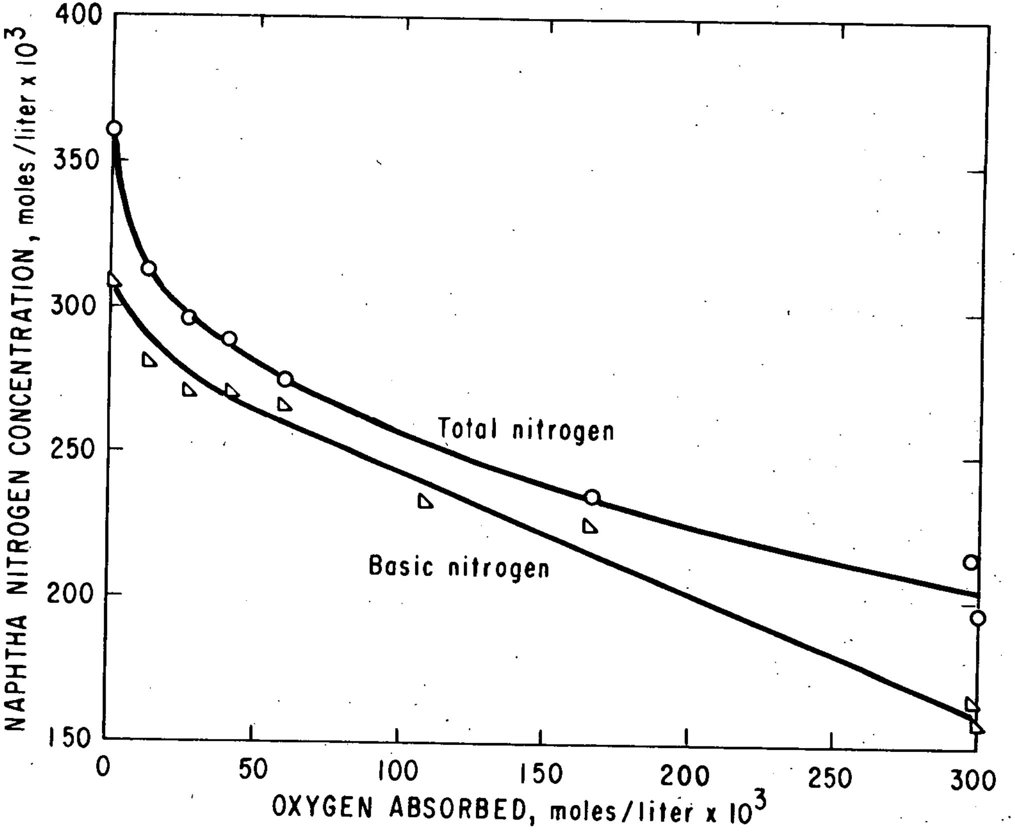

FIGURE 2.-Effect of Oxidation on Nitrogen Concentration in Shale-Oil Naphtha Fraction.

SOA-529 P

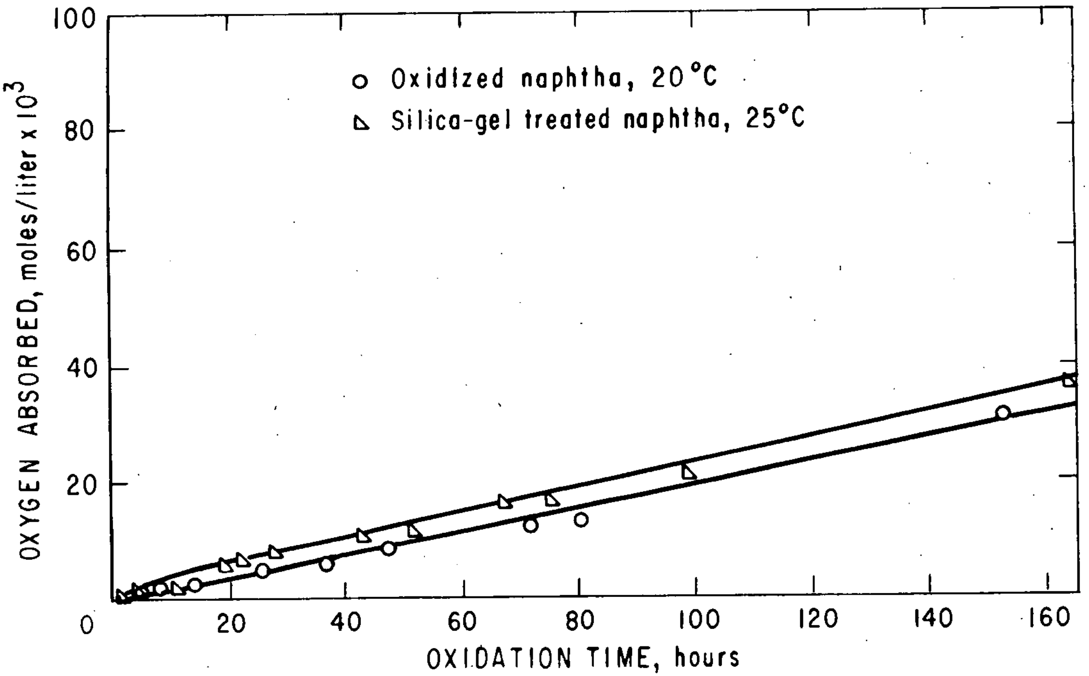

FIGURE 3.-Oxygen Absorption Curves for Oxidized Shale-Oil Naphtha Fraction, And by Shale-Oil Naphtha Fraction After Silica-Gel Treatment.

SOA-531 P

CATALYTIC REFORMING OF HYDROGENATED SHALE OIL NAPHTHA

By

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INTRODUCTION

Catalytic reforming is a process for converting low-octane naphthas or gasolines into high-octane products. Most catalytic reforming processes require very clean feedstocks to avoid deactivating the catalysts. Raw shale-oil naphthas produced during retorting or by subsequent thermal cracking of the crude shale oil have poor color and oxidation stability; they turn dark in color and form large amounts of gum soon after they are prepared. Their instability and their high contents of sulfur and nitrogen compounds make them unsuitable as feedstocks to modern noble-metal catalytic reforming processes.

To overcome the problems associated with upgrading shale-oil naphthas, production of stable naphthas by catalytic hydrogenation of crude shale oil or by coking of crude shale oil, followed by hydrogenation of the coker distillate, has been investigated (1,6). A few results on catalytic reforming of naphtha from hydrogenated coker distillate have been published (6), but little information has been published on catalytic reforming of the naphtha obtained by hydrogenating crude shale oil. The present study was undertaken to provide information on reforming the naphtha from hydrogenated crude over a broad range of reforming temperatures and pressures.

Cyclohexane was reformed at the same conditions as those used for the hydrogenated shale-oil naphtha so a comparison could be made between the results obtained with the hydrogenated naphtha and those obtained with this good reforming feedstock.

LABORATORY PROCEDURES

Naphtha Feedstock Preparation

Shale oil was prepared by the gas-combustion process from Green River oil shale at the Bureau of Mines facility near Rifle, Colo. (10). The oil was filtered to remove spent shale dust and was separated from water by decantation and distillation. It was then hydrogenated in a once-through operation with a cobalt-molybdenum-carrier catalyst at a temperature of 790°F, a pressure of 1,000 psig, a liquid hourly space velocity (LHSV) of 0.1 volume of oil per volume of catalyst per hour, and a hydrogen feed rate of 6,000 scf/bbl. The hydrogenation removed over 90 percent of the nitrogen and sulfur from the oil. The hydrogenated oil was fractionated with a true boiling point apparatus, and the fraction that distilled between 160° and 400°F was further hydrogenated with a nickel tungsten catalyst at a temperature of 700°F, pressure of 1,500 psig, LHSV of 1.0, and hydrogen feed rate of 5,000 scf/bbl to reduce its nitrogen content to 7 ppm and its sulfur content to less than 0.001 weight percent. The light ends of the liquid product from the second hydrogenation step were distilled off with a cut point of 160°F, and the higher boiling portion of this product (amounting to 32 volume-percent of the crude oil) was used as the hydrogenated naphtha feedstock.

The two-stage hydrogenation procedure was used because earlier experiments had shown that naphtha with a nitrogen content of less than 50 ppm was not produced in a single stage with either catalyst. The cobalt molybdate catalyst produced lower catalyst deposits than the nickel tungsten catalyst when hydrogenating crude shale oil, but the nickel tungsten catalyst appeared to effect better nitrogen removal in the second stage where a relatively clean naphtha feed was used. Thus, the two-stage hydrogenation with two catalysts appeared more desirable than a two-stage hydrogenation using the same catalyst in both stages.

Variables of Reforming

The experiments described here were made for the purpose of evaluating hydrogenated shale-oil naphtha as a feedstock for established reforming processes. However, finding the best operating conditions for a process is an important part of research; failure to properly control the operating variables may result in an uneconomical process. In the instance of reforming, variables such as those shown in table 1 determine the yield and quality of the products (7).

An exhaustive investigation of the reforming variables was not possible with the small laboratory-size quantities of feedstock that were available, so a selection of the variables to be investigated was necessary. Changes in temperature and pressure have more pronounced effects on the yield and quality of products than changes in the other variables; therefore, to approximate the best set of operating conditions with a commercial reforming catalyst, preselected ranges of temperature and pressure within the usual commercial reforming ranges were chosen for investigation, with the other variables held constant. Of the two variables, temperature and pressure, a proper selection of operating temperature is probably more important. As the temperature is increased, the equilibrium is shifted toward an increase in the production of aromatics; also, hydrocracking is increased. Operation under hydrogen pressure is necessary because at low pressure catalytic activity is quickly lost owing to coke formation. As the partial pressure of hydrogen is lowered, hydrocracking rates and gasoline yields decrease; aromatization rates, octane number, and hydrogen production increase.

Apparatus and Operating Procedure

Figures 1 and 2 show the flow diagram and the equipment of the reforming unit. The reactor was the fixed-bed type, equipped for downward flow, with an internal diameter of 5/16 inch, an outside diameter of 9/16 inch, and an internal length of 38.5 inches. The reactor was charged with 8.6 ml of catalyst in the form of 1/16-inch extrusions. The catalyst occupied 6.9 inches of the reactor length, and the bottom of the catalyst bed was approximately 8.5 inches from the bottom of the reactor. The upper part of the reactor was used to preheat the feed and hydrogen. The reactor was inserted in a 36- by 3-inch aluminum cylinder that was heated by a four-element furnace controlled by a four-point electronic controller.

Temperatures were measured by eight thermocouples in two vertical thermowells in the aluminum cylinder next to the reactor. The thermocouples were spaced at 3.5-inch intervals along the length of the reactor with the bottom thermocouple 5 inches above the bottom of the reactor and the top thermocouple 9 inches from the top of the reactor. Only the temperatures measured by the three thermocouples in the catalyst region were used for the reaction temperatures.

For convenience, hydrogen (99.9+ pct purity) from standard shipping cylinders was substituted for the highly concentrated hydrogen recycle gas that is normally used, to keep coke laydown on the catalyst to a minimum. At the beginning of each run, before liquid feed was started, the system was pressurized with helium, and helium was fed through the system at a slow rate for several hours while the furnace was heating the reactor to reaction temperature. After the reactor reached the desired reaction temperature, the helium was replaced by hydrogen and the feed pump was started. The feed was pumped by a positive displacement pump at the rate of 25 cc/hr, and the hydrogen was metered through a rotameter at the rate of 3,000 scf/bbl. After passing through the reactor, the oil and gas were cooled through a double-pipe heat exchanger and then passed into a low-pressure receiver. Outlet gases were reduced to atmospheric pressure, metered through a positive-displacement dry meter, and stored in a small stainless steel tank from which samples were taken for analysis. The liquid product was separated into stable and heavy reformates at a cut point of 400°F at 760 mm pressure using a Vigreux column and a condenser. There was a trace of heavy reformate in all samples.

A total of 27 tests was run. The first nine tests were run while some minor revisions to the new equipment were being made, and data from these runs are not reported. Nine tests were made with cyclohexane and nine with shale-oil naphtha. All tests were carried out at a nominal LHSV of 3 volumes of oil per volume of catalyst per hour and a hydrogen feed rate of 3,000 scf/bbl. The experiments were run for onstream test periods of 17 to 24 hours, with total throughputs of 50 to 70 volumes of feed per volume of catalyst. Operating pressures of 200, 400, and 600 psig were used at nominal temperatures of 850°, 875°, and 900°F. The furnace surrounding the reactor permitted the tests to be made essentially isothermally. Specific details for the individual runs are given in tables 2 and 3.

Catalyst

The catalyst was commercial platinum-on-silica-alumina in the form of 1/16-inch-diameter extrusions. It had been treated with a halide during manufacture to promote acid-catalyzed reforming reactions. Fresh catalyst was used for each reforming run.

RESULTS AND DISCUSSION

Catalytic reforming improved the quality of motor fuel rather than its yield. Reforming differs from cracking processes because the charge stocks are already in or near the boiling range of gasoline (6). The main reactions of catalytic reforming are shown in figure 3 (9).

Several samples of the stable reformate were submitted for mass spectral group-type analysis. The method, which is limited to samples of low olefin content (3 percent or less), determines six classes of hydrocarbons: Paraffins, monocycloparaffins, dicycloparaffins, alkylbenzenes, indanes and tetralins, and naphthalenes. The analytical results are presented in table 3 and shown graphically in figure 4.

From the mass spectral group-type analysis, it is apparent that naphthene dehydrogenation is the dominant reaction. This occurs more easily with an increase in temperature and a decrease in pressure, and it increases the octane number by a very noticeable extent.

The paraffin carbon numbers and the alkylbenzene carbon numbers were also determined from the spectral group-type analysis. These numbers are the average number of carbon atoms per molecule in the straight chain paraffins and the alkylbenzenes. The spectral analyses in table 3 show that the average paraffin carbon number decreased in all but one run and the mole percent of paraffins increased in all runs. This indicates that there was some hydrocracking of the large straight chain paraffins into smaller straight chain paraffins. Hydrocracking makes shorter paraffins which have a higher octane, but severe hydrocracking is undesirable because it gives poor yields caused by the light gases that it makes.

A composite sample of the spent catalyst from all of the reforming runs with hydrogenated naphtha was analyzed and found to contain 1.12 weight-percent hydrogen, 4.76 weight percent carbon, and 87.23 weight percent ash. Most of the carbon probably came from cracking of the feedstock.

Figures 5-A and 5-B show that as temperature was increased the API gravity decreased, but the increase of cracking, ignoring other changes in composition, should have made the API gravity increase. The decrease was probably caused by the increase of aromatics as shown in figures 5-C and 5-D.

Figure 6 shows that as temperature increases the product yield decreases quite rapidly and the octane increases quite rapidly. Aromatics have very high octane numbers, and a comparison of figures 5-C and 5-D with figures 6-C and 6-D, and an examination of the mass spectral analyses, show that the increase in octane was caused mostly by an increase in aromatics.

The optimum operating condition for each pressure occurs at the point where the yield-octane number, defined as the product of the volume-percent yield and the octane number divided by 100, is at a maximum. Yield-octane numbers were calculated for the reforming experiments and are given in tables 2 and 3 and figure 7.

The best quality reformate, with an 89 clear research octane number and a yield of 79.9 volume percent, had the highest yield-octane number (71.1) and was obtained at the highest temperature (900°F) and lowest pressure (200 psig). This suggests that the optimum operating condition would be at a higher temperature than those investigated. At the higher temperatures, octane numbers would be expected to increase further but would eventually level off while gas production would continue to increase, causing the curve for yield-octane number versus temperature to go through a maximum and curve downward. The limited amount of feedstock available did not permit the determination of the temperatures at which these effects would occur.

To determine where the curves should be drawn in figures 5, 6, and 7, all nine sets of data in each part of each figure were used to derive one equation of the form (4):

$$Y = A + bt + cP + d\,\frac{P}{t}$$

where Y = dependent variable
t = temperature, °F
P = pressure, psig
a,b,c,d = constants

Thus, the data obtained at all three pressures influenced the position of each curve at any one pressure. For this reason the curve at any individual pressure does not necessarily go through the data points for that particular pressure. Although temperature and pressure had considerable effect on the dependent variables, the interaction terms ($d\,\frac{P}{t}$) in the equations had little effect.

SUMMARY AND CONCLUSIONS

Good quality reformates were produced from the naphtha prepared by hydrogenation of crude shale oil. The best quality reformate was produced at 900°F and 200 psig, which were the highest temperature and lowest pressure tested. This reformate had a clear research octane number of 89 and a yield of 80 volume percent. Results indicated that a higher operating temperature might give a better yield octane relationship.

ACKNOWLEDGMENTS

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TABLE 1. - Reforming variables

Catalyst
Pressure
Temperature
Space velocity
H_2/naphtha ratio
Time
Naphtha
Impurities (S,N,O, metals)
Regeneration
Startup procedure

TABLE 2. - Operating conditions, product yields, and properties of liquid products for catalytic reforming of cyclohexane

Run number	Feed	10	11	12	16	17	18	13	14	15
Temperature, ° F:										
Average	-	849	875	899	843	874	901	854	879	907
Maximum	-	862	891	910	862	888	915	864	889	922
Pressure, psig	-	200	200	200	400	400	400	600	600	600
LHSV, V_f/V_c/hr[1/]	-	2.94	3.07	2.92	2.92	2.93	2.94	2.94	2.94	2.93
Throughput, V_f/V_c	-	69.47	65.70	61.76	59.48	57.72	65.36	64.33	65.53	63.49
Moles hydrogen feed/mole liquid feed	-	2.43	2.43	2.43	2.43	2.43	2.43	2.43	2.43	2.43
Hydrogen feed, scf/bbl	-	3000	3000	3000	3000	3000	3000	3000	3000	3000
Hydrogen produced, scf/bbl	-	2895	3028	3089	2085	2299	2464	1132	1575	1702
Hydrogen produced, wt pct of feed	-	5.62	5.88	5.99	4.05	4.46	4.78	2.20	3.06	3.30
Liquid yield, vol pct of feed	-	76.86	76.66	75.98	80.99	80.30	79.30	86.30	85.95	85.35
Liquid yield, wt pct of feed	-	84.78	84.99	84.24	85.13	84.61	84.17	85.74	86.61	85.67
Research octane number, clear	85	103	105	109	96	96	98	89	90	88
Research octane number, with 3 cc TEL/gal	97	111	112	113	106	107	108	101	103	102
Yield-octane, vol fraction x R.O.N., clear	-	79.2	80.5	82.8	77.8	77.1	77.7	76.8	77.4	75.1
Properties of stable reformate:										
Specific gravity, 60°/60° F	0.782	0.863	0.867	0.867	0.822	0.824	0.830	0.778	0.785	0.788
Gravity, ° API	49.4	32.5	31.7	31.7	40.6	40.2	39.0	50.4	48.8	48.1
Average molecular weight	84	75	76	77	76	75	74	78	78	73
Characterization factor, K	11.0	10.0	9.9	9.9	10.4	10.4	10.3	11.0	10.8	10.9
Heat of vaporization, Btu/lb	155	170	169	168	165	166	167	158	160	163
ASTM distillation, ° F:										
IBP	176	169	169	168	161	160	158	159	156	146
10 pct recovered	177	173	172	172	165	165	165	161	161	157
50 pct recovered	177	174	174	175	167	167	168	163	163	161
90 pct recovered	177	177	177	177	171	173	174	166	168	169
End point	178	187	201	193	161	162	179	179	199	179
Rec., vol pct	99.0	99.0	99.0	99.0	98.0	98.0	99.0	99.0	99.0	98.0
Res., vol pct	nil	nil	nil	nil	nil	nil	nil	nil	nil	nil
Loss, vol pct	1.0	1.0	1.0	1.0	2.0	2.0	1.0	1.0	1.0	2.0
Carbon, wt pct	85.72	-	-	92.04	-	-	-	87.14	85.43	87.62
Hydrogen, wt pct	14.28	-	-	8.00	-	-	-	12.55	12.86	11.84

[1/] Volume of feed/volume of catalyst/hour.

TABLE 3. - Operating conditions, product yields, and properties of liquid products for catalytic reforming of hydrogenated naphtha

Run number	Feed	19	20	21	25	26	27	22	23	24
Temperature, ° F:										
Average	-	847	871	903	849	875	900	844	876	904
Maximum	-	860	886	917	860	887	912	856	884	915
Pressure, psig	-	200	200	200	400	400	400	600	600	600
LHSV, V_f/V_c/hr	-	2.99	3.00	2.98	2.99	2.96	2.96	2.99	2.98	2.99
Throughput, V_f/V_c	-	68.32	70.92	70.36	52.74	51.33	55.86	60.39	59.99	55.14
Moles hydrogen feed/mole liquid feed	-	3.50	3.50	3.50	3.50	3.50	3.50	3.50	3.50	3.50
Hydrogen feed, scf/bbl	-	3000	3000	3000	3000	3000	3000	3000	3000	3000
Hydrogen produced, scf/bbl	-	1184	1459	1756	1219	1179	1497	818	1218	1393
Hydrogen produced, wt pct of feed	-	2.24	2.91	3.50	2.43	2.35	2.98	1.63	2.43	2.77
Liquid yield, vol pct of feed	-	87.80	84.32	79.90	88.38	85.40	81.95	90.60	85.91	82.20
Liquid yield, wt pct of feed	-	91.02	87.89	84.41	91.28	88.31	85.18	92.38	88.39	85.00
Research octane number, clear	40	69	78	89	70	79	85	59	70	82
Research octane number, with 3 cc TEL/gal	64	88	94	99	89	92	97	80	88	95
Yield-octane, vol fraction x R.O.N., clear	-	60.6	65.8	71.1	61.9	67.5	69.7	53.4	60.1	67.4
Properties of stable reformate:										
Specific gravity, 60°/60° F	0.762	0.790	0.794	0.805	0.787	0.788	0.792	0.777	0.784	0.788
Gravity, ° API	54.2	47.6	46.7	44.3	48.3	48.1	47.2	50.6	49.0	48.1
Average molecular weight	118	108	110	108	119	116	110	119	117	111
Characterization factor, K	11.9	11.4	11.3	11.2	11.5	11.4	11.4	11.6	11.5	11.4
Heat of vaporization, Btu/lb	130	140	138	140	133	133	137	131	133	136
ASTM, distillation, ° F:										
IBP	225	161	153	148	179	144	137	177	180	142
10 pct recovered	256	218	230	220	243	226	220	242	238	214
50 pct recovered	297	290	288	285	294	287	283	293	291	277
90 pct recovered	350	352	350	340	350	348	344	350	350	342
End point	371	390	406	411	391	394	395	383	389	397
Rec., vol pct	99.0	97.0	98.0	98.0	99.0	98.0	98.0	98.0	98.0	99.0
Res., vol pct	nil	nil	nil	nil	nil	nil	nil	nil	nil	nil
Loss, vol pct	1.0	3.0	2.0	2.0	1.0	2.0	2.0	2.0	2.0	1.0
Carbon, wt pct	85.90	87.30	87.29	86.16	86.90	87.28	87.60	86.10	86.92	87.24
Hydrogen, wt pct	14.02	12.69	12.44	13.30	12.92	12.68	12.24	13.32	12.92	12.67
Nitrogen, ppm	7.14	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Sulfur, wt pct	<0.001	-	-	-	-	-	-	-	-	-
Alkylbenzene carbon number	8.40	8.44	8.01	8.24	7.72	7.98	7.95	8.17	8.14	-
Paraffin carbon number	8.87	8.99	8.81	8.68	8.59	8.30	8.10	8.59	8.48	-
Hydrocarbons, mole pct:										
Paraffins	42.1	53.9	50.9	47.9	59.5	55.2	49.9	61.8	62.7	-
Monocycloparaffins	38.4	0.3	2.1	0	1.3	1.7	0.5	9.0	5.7	-
Dicycloparaffins	7.0	0.7	0.1	0.2	0.8	0.3	0.3	1.2	0.7	-
Alkylbenzenes	9.1	41.4	42.3	48.8	37.2	41.7	48.7	26.6	28.5	-
Indanes-tetralins	1.7	1.9	3.0	2.0	0.4	0.6	0.2	0.7	1.7	-
Naphthalenes	1.7	1.8	1.6	1.1	0.8	0.5	0.4	0.7	0.7	-

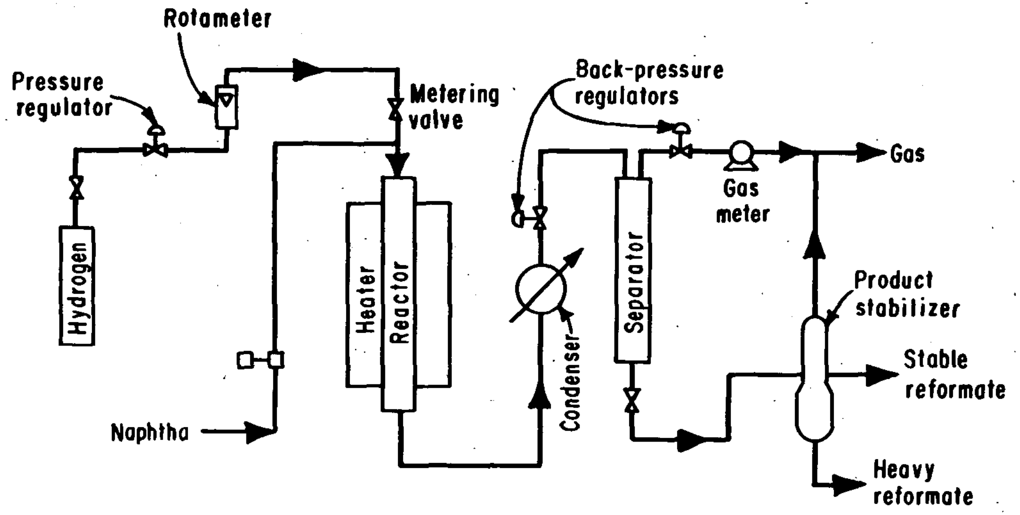

Rotameter
Pressure regulator
Metering valve
Back-pressure regulators
Hydrogen
Heater
Reactor
Naphtha
Condenser
Separator
Gas meter
Gas
Product stabilizer
Stable reformate
Heavy reformate

FIGURE 1.-Simplified Flow Diagram of Catalytic Reforming Unit.

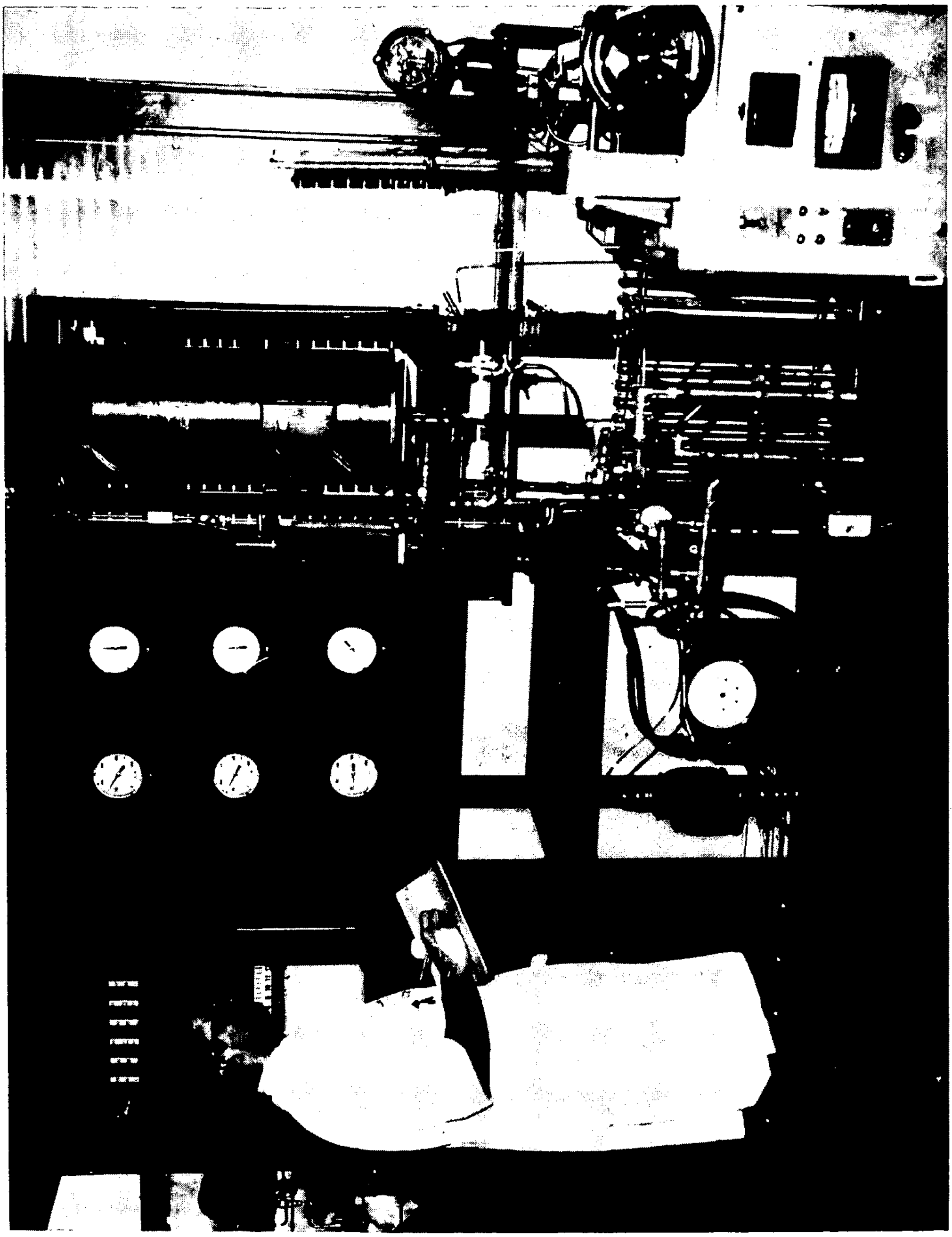


Figure 2.

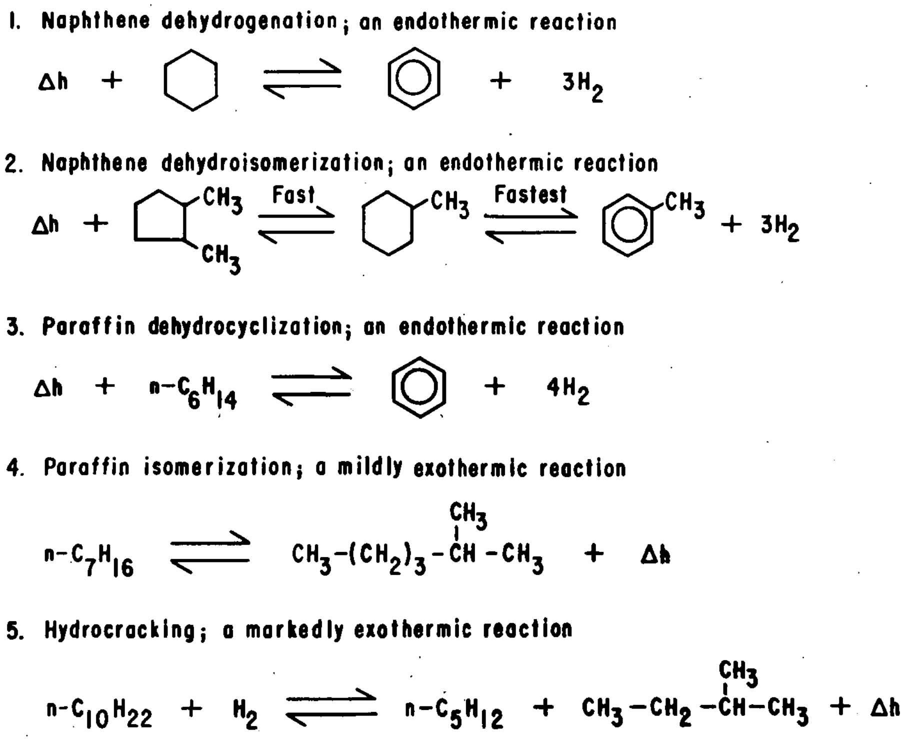
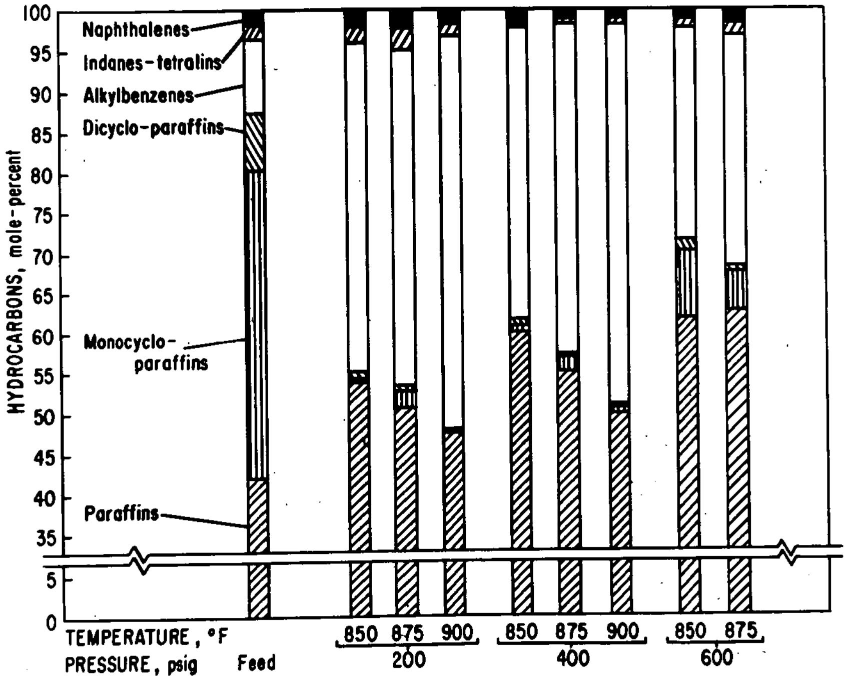

1. Naphthene dehydrogenation; an endothermic reaction
Δh + ⇌ + 3H2
2. Naphthene dehydroisomerization; an endothermic reaction
Δh + CH3 CH3 Fast CH3 Fastest CH3 + 3H2
3. Paraffin dehydrocyclization; an endothermic reaction
Δh + n-C6H14 ⇌ + 4H2
4. Paraffin isomerization; a mildly exothermic reaction
n-C7H16 ⇌ CH3-(CH2)3-CH-CH3 + Δh
CH3
5. Hydrocracking; a markedly exothermic reaction
n-C10H22 + H2 ⇌ n-C5H12 + CH3-CH2-CH-CH3 + Δh
CH3

FIGURE 3.-Catalytic Reforming Reactions.



Feedstock: hydrogenated naphtha

Figure 4.- Effect of Temperature and Pressure on Product Analysis.

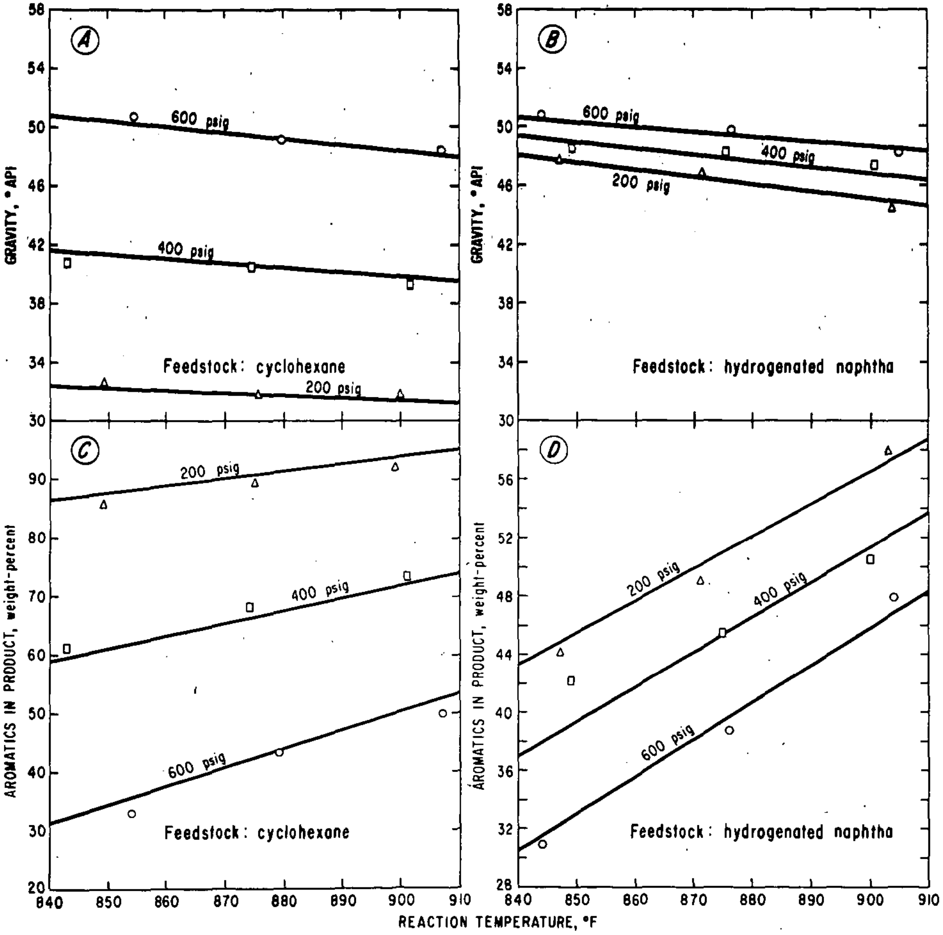


FIGURE 5.-Effect of Temperature and Pressure on Results from Catalytic Reforming.

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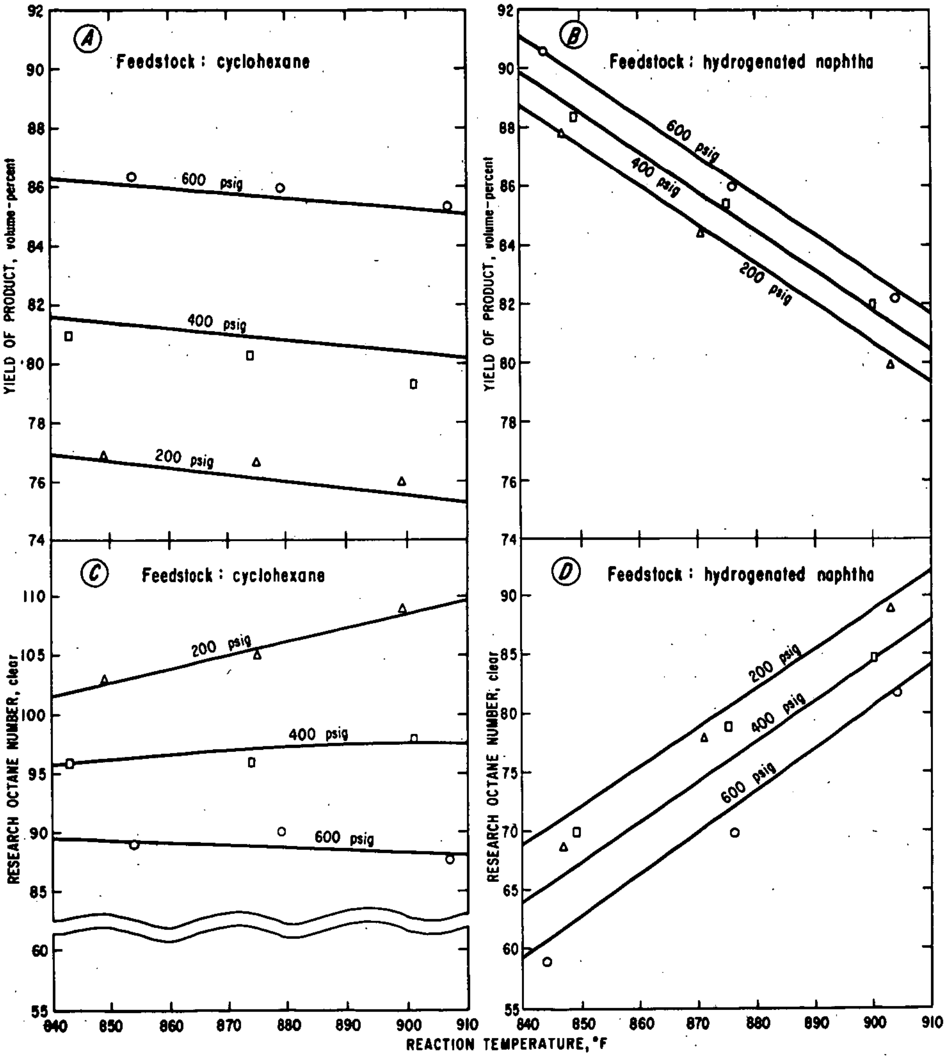

FIGURE 6.-Effect of Temperature and Pressure on Results from Catalytic Reforming.

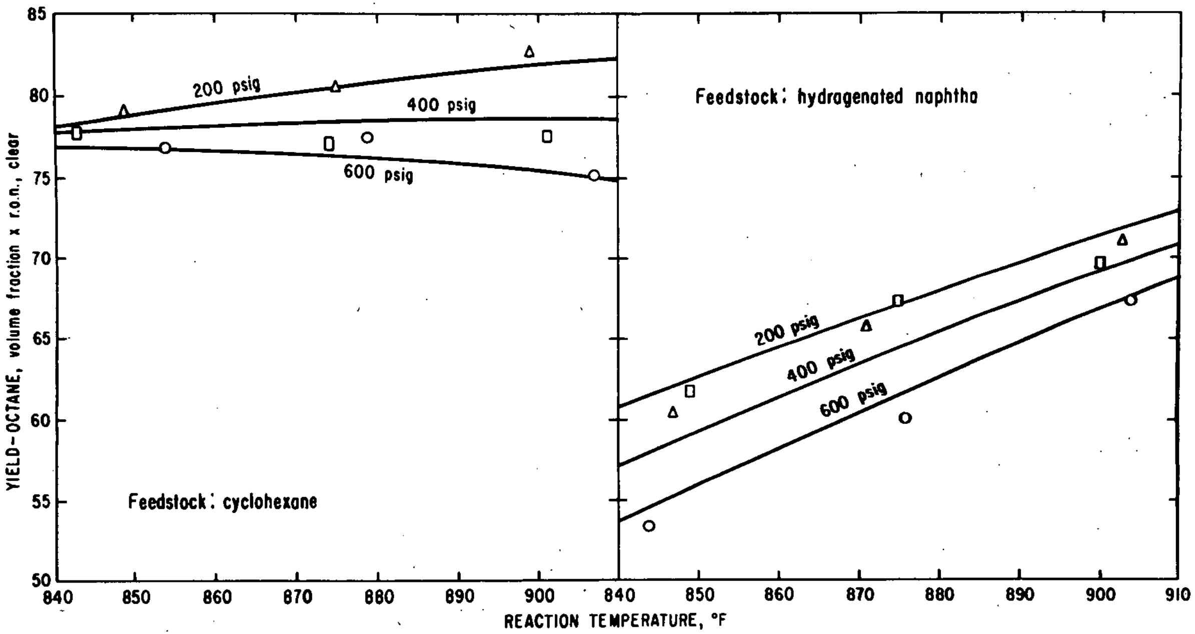

FIGURE 7.-Effect of Temperature and Pressure on Yield-Octane from Catalytic Reforming.

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